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# RISKCYCLE (#226552)

Deliverable 5.1. Definition of risk scenarios and historical analysis

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Prof. Dr.-Ing. habil. Dr. h.c. Bernd Bilitewski

Dresden University of Technology
Institute of Waste Management and Contaminated Sites Treatment

**Responsible of WP 5 : Polytechnic University of Catalonia. Partner 4.**

Deliverable 5.1. due to 31st of May 2010.

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## Nomenclature

| | |
|---|---|
| APFO | Perfluoroctanoate ammonium salt |
| B | Bioaccumulative |
| BCF | Bioconcentration Factor (e.g. Concentration of the substance in the fish / Concentration of the substance in the water) |
| bwt | Body weight |
| CDT | 1,5,9-cyclododecatriene |
| CMR | Carcinogenic, Mutagenic and toxic to Reproduction |
| dw | Dry weight |
| EC | European Commission |
| $EC_{\#}$ | Effect Concentration measured as #% effect |
| ECB | European Chemicals Bureau |
| EPS | Expandable Polystyrene |
| EUSES | European Union System for the Evaluation of Substances |
| HBCDD | Hexabromocyclododecane |
| HIPS | High Impact Polystyrene |
| $K_{oc}$ | Organic carbon-water partition coefficient |
| $K_{ow}$ | Octanol water partitioning coefficient |
| LD | Lethal Dose |
| $LD_{50}$ | Median Lethal Dose |
| LOAEL | Lowest Observed Adverse Effect Level |
| LOEC | Lowest Observed Effect Concentration |
| MOS | Margin Of Safety |
| NEL | No Effect Level |
| NOAEC | No Observed Adverse Effect Concentration |
| NOAEL | No Observed Adverse Effect Level |
| NOEC | No Observed Effect Concentration |
| P | Persistence |
| PBT | Persistent, Bioaccumulative and Toxic |
| PEC | Predicted Environmental Concentration |
| PFBuS | Perfluorobutanesulfonate |
| PFC | Perfluorinated coumponds. |
| PFCA | Perfluorocarboxilic acids |
| PFDA | Perfluorodecanoic acid |
| PFDS | Perfluorodecanesulfonate |
| PFHpA | Perfluoroheptanoic acid |
| PFHxA | Perfluorohexanoic acid |
| PFHxS | Perflurohexanesulfonate |

| | |
|---|---|
| PFNA | Perfluorononanoic acid |
| PFO | Perfluorooctanoate salt |
| PFOA | perfluorooctanoic acid |
| PFOS | Fluorooctanoicsulfonate |
| PFOSA | Perfluorooctanesulfonamide |
| PFTDA | Perfluorotetradecanoic acid |
| PFUnDA | Perfluoroundecanoic acid |
| PNEC | Predicted No Effect Concentration |
| PS | Polystyrene |
| PTDI | Provisional Tolerable Daily Intake |
| PTFE | Polytetrafluoroethylene |
| STP | Sewage Treatment Plant |
| T | Toxic |
| TGD | Technical Guidance Document |
| THPFOS | 1H,1H,2H,2H-perfluorooctanesulfonic acid |
| vPvB | very Persistent and very Bioaccumulative |
| XPS | Extruded Polystyrene |

# 1 Justification

This document presents the first deliverable of Riskcycle workpackage 5 (Deliverable 5.1). It shows the outcome of the work carried out by WP5 partners: TUD, CSIC, URV, USCS, BRGM and UPC. This work has been done during the first 9 months of the Riskcycle project (September 2009- May 2010).

As stated in the Riskcycle DOW (Description of Work), task 1 of WP5 entailed defining diverse risk scenarios for additives used in six different industrial sectors: textile, electronics, plastics, leather, paper and lubricants.

There exist thousands of additives used in the selected sectors. For this reason, after the Kick-off meeting of Riskcycle project in Barcelona, it was decided that the best way to approach such a broad field of study was dividing the different sectors among the different workpackages (WP). If each WP was in charge of one of these sectors, it would be much easier to study in detail the additives used in them. By doing so, a previous selection of additives could be done in order to focus the project for the future. According to this approach, “Textile Sector” was assigned to WP5.

The partners involved in this WP did a preliminary revision of all the additives used in the textile sector and from here, the most interesting substances (from the environmental and human health point of view) were identified. A study in depth of these additives was carried out and risk scenarios for these substances were designed. The results were presented at Hanoi Workshop.

UPC is the leader of this workpackage and therefore the responsible of preparing this document. However, this would have not been possible without the data contribution of the aformentioned partners.

# 2 Introduction

## 2.1 *Research approach*

This report focuses on the potential harm that additives used in the production and manufacture of textiles may have on the environment and human health once the product is finished. Additives are chemicals added in small amounts to other substances or materials to improve their properties in some way.

This work has been done within the framework of WP5 of RISKCYCLE project and includes the contributions provided by the different WP members.

A thorough survey of literature has been performed to identify the diverse processes and products which can play a role in the textile sector. Their potential harmful action on the environment and on human health has also been analysed. Taking into consideration all this information, a selection of the most representative additives has been carried out.

The significant environmental impact caused by these chemicals can be related to the production process as well as the finished product itself. The **process dimension** is attributed to the performance of the process itself from an environmental point of view, i.e. the harm of chemicals used during the production process. The **product dimension** refers to the influence of the process on the product's performance (i.e. its use, disposal or recycling).

In the textile sector most of the chemicals are applied during the finishing process. This process enhances the appearance, durability and serviceability of fabrics (OECD, 2004) and it involves different steps: fabric pre-treatment (desizing, washing, scouring, bleaching, etc.), colouring (dyeing and/or printing) and functional finishing (e.g. flame retardant or waterproof finishes).

Different environmental impacts are related to the process dimension. For instance, textile industries have a high demand of water, and their effluents may contain high concentrations of pollutants of potential harmful in the environment. Effluents from textile factories usually need treatment before its release to the environment and they are characterized by: high BOD, solids in suspension, substances from dyes, metals (Pb, Ni, Cu, Cd, Cr) and organic compounds (phtalates and phenols) (Correia et al., 1994; Rutherford et al., 1992; Chen et al., 2001; Sponza, 2002; Hai and Yamamoto, 2006; Gómez et al., 2008; Ali et al, 2009; Jadhav et al., 2010; Tastan et al., 2010).

On the other hand, the environmental impact of the product is mostly related to the lifetime of the article but also to the performance in other stages of the life cycle, e.g. performance during use, disposal and recycling (EEA, 1997).

According to the approach followed in RISKCYCLE, chemicals to be assessed are those involved in the disposal and recycling of the textile products. Therefore, RISKCYCLE project focuses on the environmental performance of textiles within the product dimension rather than within the process dimension. This is the reason why the following sections are mainly devoted to the description of the major finishing chemicals used in the textile industry (functional finishers and colorants, section 4). These finishing chemicals are the ones present in the final product and as a consequence they can produce environmental or health damage during the disposal and recycling of the textiles. Chemicals used during the most common pre-treatment processes of textiles are also presented in section 3 although they are not part of the final product.

In section 5, a selection of chemical substances is presented and proposed in order to continue with the development of the research on additives used in textile products.

Finally, in sections 6, 7 and 8 the three selected substances are analyzed in depth and risk scenarios for each of them are presented.

## 2.2 *Textile Sector*

The textiles sector prepares natural and man-made materials for use in clothing, carpets, furniture manufacture, interior decoration, etc. Natural and man-made fibres are spun into yarns and threads, woven or knit into fabrics, and finished and sewed into final products (Graedel and Howard-Grenville, 2005). The most common technique for manufacturing fabrics is weaving, in which one set of yarns is interlaced with another set oriented crosswise on a loom. Before weaving, the yarn is passed through a sizing solution to protect it from snagging or abrasion. An alternative fabric manufacture technique is knitting, in which the yarn threads are interlocked (Graedel and Howard-Grenville, 2005).

In accordance with the World Trade Organisation (WTO), manufactured textile products can be divided into two basic sub-sectors: textiles and clothing. The textiles sub-sector includes carpets, furnishing and upholstery fabrics, household linen, and also technical textiles, such as textiles for construction, agriculture, vehicles, packing, etc. The clothing sub-sector includes the woven fabrics and knitted fabrics for sportswear, rainwear, fashion articles, work wear, etc. In agreement with this division, the economic movements (exports in million US dollars) of textiles and clothing are shown in Table 1 for a group of selected regions, according to data of 2008.

Leading exporters are also shown in Table 2. Although these figures do not indicate the current material flow, they may be taken as approximate values for the calculation of the amount of textile and clothing products (in mass units). Figure 1 shows schematically the values of Table 1 on the world map.

**Table 1. Textile and clothing exports of selected regions by destination, 2008. Source: WTO (2010)**

| Sub-sector | Destination region | Million US $ | % |
|---|---|---|---|
| Textiles | Africa | 16469 | 6.6 |
| | Asia | 63104 | 25.2 |
| | Australia and New Zealand | 2860 | 1.1 |
| | Europe | 95950 | 38.3 |
| | Middle East | 16751 | 6.7 |
| | North America | 32643 | 13.0 |
| | South and Central America | 13642 | 5.5 |
| | *Total World Exportation* | *250198* | *100.0* |
| Clothing | Africa | 6686 | 1.8 |
| | Asia | 45965 | 12.7 |
| | Australia and New Zealand | 4363 | 1.2 |
| | Europe | 180227 | 49.8 |
| | Middle East | 13127 | 3.6 |
| | North America | 82837 | 22.9 |
| | South and Central America | 7911 | 2.2 |
| | *Total World Exportation* | *361888* | *100.0* |

**Table 2. Leading exporters of textiles and clothing, 2008. Source: WTO (2010)**

| Sub-sector | Country/Region | Million US $ | % | Sub-sector | Country/Region | Million US $ | % |
|---|---|---|---|---|---|---|---|
| Textiles | European Union (27) | 80207 | 32.1 | Clothing | China | 119978 | 33.2 |
| | China | 65256 | 26.1 | | European Union (27) | 112375 | 31.1 |
| | United States | 12496 | 5.0 | | Hong Kong, China | 27908 | 7.7 |
| | Hong Kong, China | 12256 | 4.9 | | Turkey | 13591 | 3.8 |
| | Korea, Republic of | 10371 | 4.1 | | Bangladesh | 10920 | 3.0 |
| | India | 10267 | 4.1 | | India | 10854 | 3.0 |

| Sub-sector | Country/Region | Million US $ | % | Sub-sector | Country/Region | Million US $ | % |
|---|---|---|---|---|---|---|---|
| | Turkey | 9399 | 3.8 | | Viet Nam | 8971 | 2.5 |
| | Taipei, Chinese | 9220 | 3.7 | | Indonesia | 6285 | 1.7 |
| | Japan | 7340 | 2.9 | | Mexico | 4911 | 1.4 |
| | Pakistan | 7186 | 2.9 | | United States | 4449 | 1.2 |
| | United Arab Emirates | 5751 | 2.3 | | Thailand | 4241 | 1.2 |
| | Indonesia | 3675 | 1.5 | | Pakistan | 3906 | 1.1 |
| | Thailand | 3211 | 1.3 | | Tunisia | 3766 | 1.0 |
| | Mexico | 1993 | 0.8 | | Cambodia | 3645 | 1.0 |
| | Canada | 1988 | 0.8 | | Malaysia | 3624 | 1.0 |
| | Switzerland | 1802 | 0.7 | | Sri Lanka | 3460 | 1.0 |
| | Viet Nam | 1639 | 0.7 | | Morocco | 3334 | 0.9 |
| | Malaysia | 1549 | 0.6 | | Honduras | 2940 | 0.8 |
| | Brazil | 1361 | 0.5 | | United Arab Emirates | 2631 | 0.7 |
| | Bangladesh | 1090 | 0.4 | | Philippines | 1979 | 0.5 |

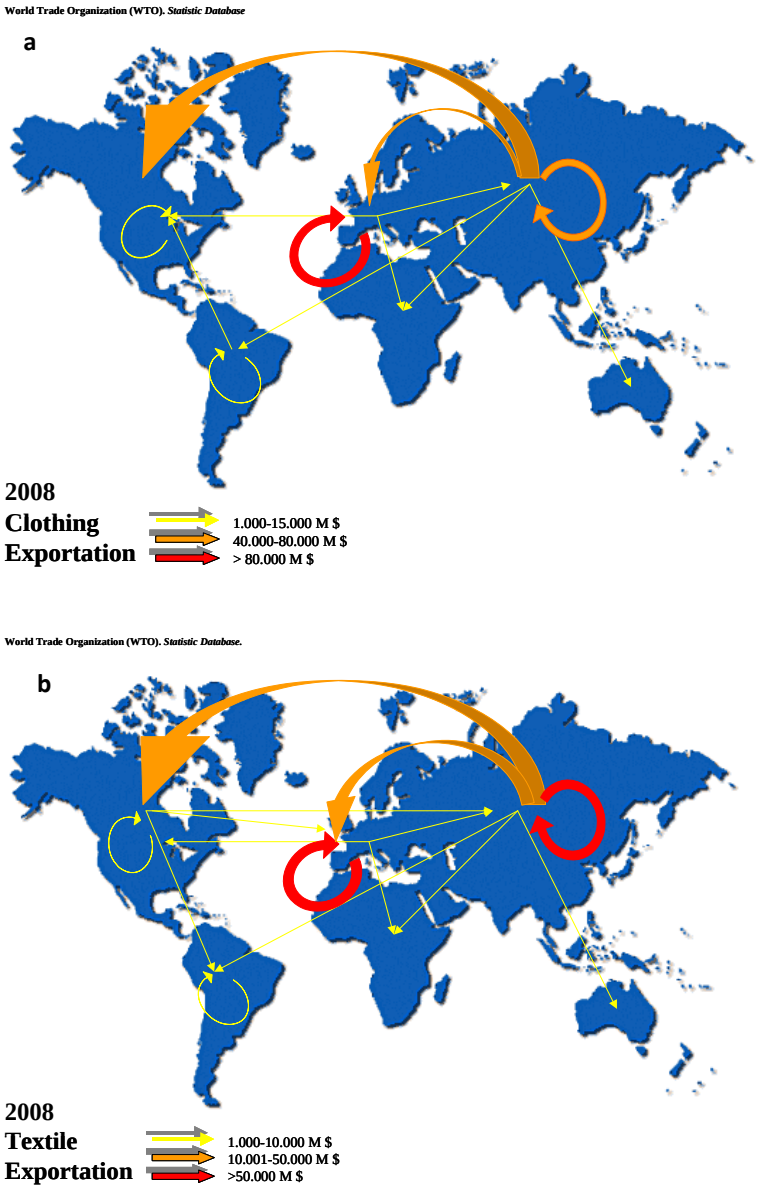


**Figure 1. World exportations diagram (million US $): (a) clothing; (b) textiles, 2008. Source: WTO (2010)**

Other classifications include that available from the United Nations Commodity Trade Statistics Database (United Nations, 2009). In this case textile products are specifically divided into floor coverings, made-up articles, and articles of apparel and clothing accessories (a distinction is made in this case between genders). Figure 2 shows imports of textile products in the world (values in million US dollars) from year 2003 to 2007, arranging them in categories according to the different types of commodity. It can be observed from this figure that over

this period the total amount of dollars spent on textile imports increased. Moreover, each year the highest percentage of money spent on textile products (around 30%) corresponded to those articles included in the group of commodities identified with number 845. This was followed by the group of commodities identified with number 842 (around 22%).

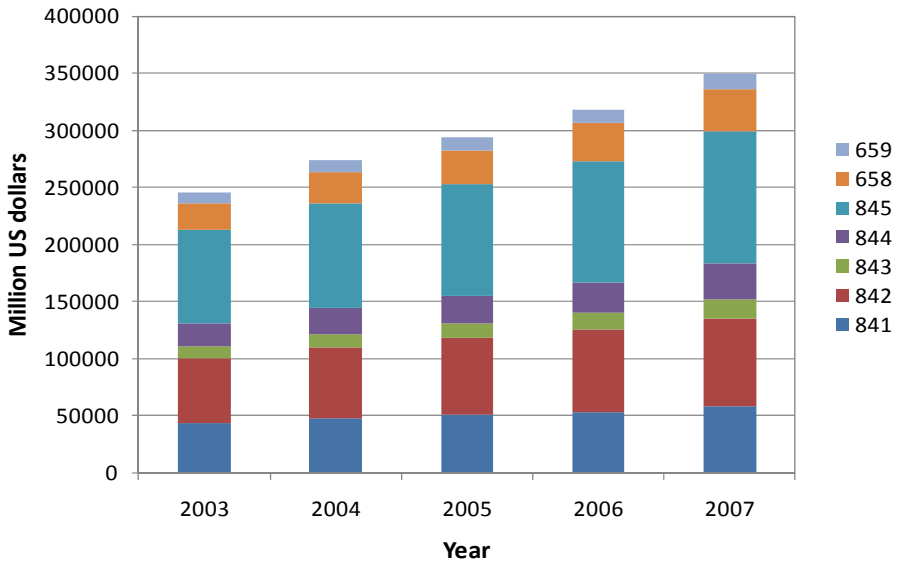


**Figure 2. Imports of textile products in the world making a distinction between the types of commodity. Source: United Nations (2009).**

**Legend:**

**659:** Floor coverings (carpets, linoleum)
**658:** Made-up articles, wholly or chiefly of textile materials (blankets, bedlinen, curtains, etc.)
**845:** Articles of apparel, of textile fabrics, whether or not knitted or crocheted (jerseys, pullovers, T-shirts, swimwear, etc.)
**844:** Women's or girls' coats, capes, jackets, suits, trousers, shorts, shirts, dresses and skirts, underwear, nightwear and similar articles of textile fabrics, knitted or crocheted (other than those of group 845)
**843:** Men's or boys' coats, capes, jackets, suits, blazers, trousers, shorts, shirts, underwear, nightwear and similar articles of textile fabrics, knitted or crocheted (other than those of group 845)
**842:** Women's or girls' coats, capes, jackets, suits, trousers, shorts, shirts, dresses and skirts, underwear, nightwear and similar articles of textile fabrics, not knitted or crocheted (other than those of group 845)
**841:** Men's or boys' coats, capes, jackets, suits, blazers, trousers, shorts, shirts, underwear, nightwear and similar articles of textile fabrics, not knitted or crocheted (other than those of group 845)

Manufactured textile products can also be divided based on their intended use. In accordance with the Öko-Text Standard 100 label (Oeko-Text Institutes, 2010) textile products can be allocated to four different product classes:

1. Textiles and textile toys for babies and toddlers: underwear, romper suits, bed-linen, bedding, stuffed toys, etc.
2. Textiles where a large part of the surface area is in direct contact with the skin: underwear, bed-linen, towels, shirts, blouses, tights, etc.
3. Textiles which do not come into contact with the skin, or for only a small part of their surface area: jackets, coats, etc.
4. Furnishing materials for decorative purposes: tablecloths, curtains, carpets, upholstery, mattresses, etc.

# 3 Pre-treatment of textiles

In pre-treatment steps natural impurities on the textile raw material, e.g. by-products on cotton as waxes, proteins etc., vegetable impurities on wool, biocides but also by-products from upstream production steps (preparation agents, sizing agents, etc.) and fibre specific by-products from man-made fibres (monomers, fibre solvents) are removed.

Mechanical, thermal and wet pre-treatment steps are used in the finishing of textiles. In comparison to thermal and wet pre-treatment processes, mechanical pre-treatment (such as brushing, cutting, etc.) is accompanied with negligible environmental charges (OECD, 2004). No chemicals are used in thermal pre-treatments (such as thermo fixation, singeing, etc.) and wet processes are carried out with water and chemicals.

As the scope of this study focuses on chemicals used in textiles finishing which fasten on the final product, and on their environmental and health impacts, wet pre-treatment processes are here only briefly described. According to OECD (2004), wet-processes in pre-treatment include: desizing, washing, scouring, mercerizing, causticizing, carbonising, crabbing and bleaching. The objective attained with these processes and the most common agents employed are described in Table 3.

**Table 3. Wet pre-treatment processes and associated agents employed in the textile industry. Source: OECD (2004); Lacasse and Baumann (2004)**

| Pre-treatment process | | Description |
|---|---|---|
| Desizing | Function | The sizing agents on the warp yarns, applied in weaving mills for better weaving efficiency, are removed before further processing. |
| | Agents | For the removal of water-soluble size: hot water (additional surfactants)<br>For the removal of water insoluble size: enzymes, mono- or dispersulphates, or sulphuric acid with wetting agents |
| Washing | Function | To remove preparation agents as spin finishes, coning-, warping- and twisting oils etc., as well as other impurities, synthetic materials are washed with water and detergents. |
| | Agents | Surfactants: non-ionic surfactants (alkyl polyglucosides), anionic (□-olefin sulphonates, □-sulpho fatty esters, dodecyl and tetradecyl alcohols), etc. |
| Scouring | Function | To extract natural impurities (waxes, pectines, proteins, metal salts) cotton fabrics and their blends are treated in a discontinuous or continuous way with hot alkali. |
| | Agents | Strong alkali, and strong alkali-resistant and electrolyte-resistant surfactants (fatty acid ethoxylates, alkylphenol ethoxylates, alkane sulphonates, complexing agents) |
| Mercerising and causticizing | Function | Mercerising is a process for increasing the tensile strength, lustre, sheen, dye affinity, and abrasion resistance of cotton goods by impregnating the fabric with sodium hydroxide solution under tension stress.<br>Similar effects to mercerising can be achieved by the causticizing process. Causticizing in comparison to mercerising is done without tension stress on the textile at temperatures between 10 °C and 15 °C. |
| | Agents | Strong alkali (sodium hydroxide, ammonia), wetting agents stable in highly concentrated lyes (low molecular weigth alkyl sulphates, alkane sulphonates), antifoaming agents as shorter-chain alkyl phosphates and complexing agents |
| Carbonising | Function | Carbonizing is a pre-treatment step for wool (loose fibres and fabrics) with the aim to destroy and remove vegetable impurities with strong acid. |
| | Agents | Strong sulphuric acid and acid-stable wetting agents (alkyl arylsulphates, alkane sulphates, fatty alcohol ethoxylates) |
| Crabbing | Function | Tensions are removed at wool fibres by means of a hot water treatment. |
| | Agents | Hot water |
| Bleaching | Function | The whiteness of the material increases and the printing and dyeing processes are improved after bleaching. The bleaching agents (peroxide, sodium chlorite, reductive |

| Pre-treatment process | Description | |
|---|---|---|
| | | agents) vary with the textile substrate. |
| | Agents | Main bleaching agents: hydrogen peroxide, sodium hypochloride, sodium chlorite, potassium permanganate, ozone, sodium dithionite, thiourea dioxide, hydroxylamine sulphate, peracetic acid. Auxiliary agents are also needed. |

A relevant environmental concern related to the bleaching process has to do with the fact that all chlorine based bleaches give rise to adsorbable organic halogen compounds (AOX) in the wastewater. Therefore, hydrogen peroxide is usually preferred for bleaching. Halogenated chemicals are often very persistent and toxic to aquatic and terrestrial organisms, whereas hydrogen peroxide decomposes, forming only oxygen and water (Kalliala and Talvenmaa, 2000). Presence of AOX in the environment is a worldwide concern as they are persistent, and reported to be carcinogenic, bioaccumulative and also have adverse effect on the flora and fauna in the aquatic system. When AOX chemicals are concentrated and released in large quantities to receiving water bodies such as lakes and rivers they can cause chronic toxicity to the aquatic organisms (Ranganathan et al., 2007).

Another specific environmental case is shown in the use of alkylphenol ethoxylates (APEO) (Castillo and Barceló, 2001). APEOs are applied in textile industries in auxiliaries' formulations (used in pre-treatment operations) or in additives as detergents or wetting agents in wool scouring, hydrogen peroxide bleaching and dyeing processes. Because of the poor degradability and toxicity of their metabolites, APEOs have been replaced in household applications in most western countries, mainly by alcohol ethoxylates. Among APEOs, nonylphenol ethoxylates (NPEOs) are by far the most commonly used isomers; 80% of the APEO surfactants used are NPEOs, while the remaining 20% are almost entirely octylphenol isomers (OPEOs). Commercial NPEOs are complex mixtures of ethoxy homologues and alkyl isomers (Loos et al., 2007).

# 4 Functional finishing and colouring of textiles

In this section chemicals used in the functional finishing and colouring of textiles are presented according to their intended use. These compounds are the ones that are prone to originate a potential environmental impact during their disposal and recycling. For this reason, the effect of these products on the environment and health is briefly discussed. Most of the information contained in this section has been extracted from Schindler and Hauser (2004).

## 4.1 *Softeners*

Softeners give textiles a soft hand, some smoothness, more flexibility and better drape and pliability. Typical softened textile articles are almost all apparel and home furnishing textiles. Main softeners used in the textile industry are indicated in Table 4.

**Table 4. Softeners**

| Chemicals | Subgroup |
|---|---|
| N,N-distearyl-N,N-dimethyl ammonium chloride (DSDMAC)<br>Quaternary ammonium salts with one or two alkyl chains<br>Amine salts<br>Imidazolines<br>Di-(stearylcarboxylethyl)-hydroxyethylmethylammonium methylsulfate<br>A triethanolamine ester quaternary | Cationic |
| Alkylsulfate salt<br>Alkylsulfonate salt | Anionic |
| Alkyldimethylamine oxide softeners<br>Betaine softeners | Amphoteric |
| Polyethylene<br>Ethoxylated fatty alcohol<br>Ethoxylated fatty acid<br>Ethoxylated fatty amide<br>Ethoxylated fatty amine (cationic at pH < 7)<br>Castor oil ethoxylate | Non-ionic |
| Polydimethylsiloxane<br>Epoxy functional silicone softener<br>Amino functional silicone softener<br>Cationic silicone softener<br>Hydrophilic silicone softener | Silicone softeners |

Ecological and toxicity problems associated with several softeners are:

1. Fish toxicity and poor biodegradability of many conventional quaternary ammonium compounds.
2. Depending on the method of synthesis of the silicone softeners, they can contain variable amounts of volatile siloxane oligomers. Together with volatile emulsifiers these oligomers can cause atmospheric pollution problems in the waste air from tenter frames.

## 4.2 *Hand building finishes*

The main effects of hand building finishes are fullness, which is the feeling of increased bulk or weight, and stiffness or resistance to bending. Examples of textiles with hand building finishes are laundered shirts, blouses, table linens, some lining, suit and costume fabrics, selected denim articles, work clothes and industrial uniforms (e.g. jeans, overalls, aprons and lab coats), mattress duck, tapestries and awning fabrics. Main hand building finishers used in the textile industry are indicated in Table 5.

**Table 5. Hand building finishes**

| Chemicals | Subgroup |
|---|---|
| Starch derivatives<br>Polyvinyl alcohol structures | Non-durable |
| Polyvinyl acetate<br>Ethylene-vinyl acetate copolymer<br>Polyvinylmethyl ether<br>Acrylic copolymers (polyacrylates and polymethacrylates)<br>Formaldehyde-containing thermosetting polymers (precondensates of urea or melamine with formaldehyde) | Durable |

Ecological and toxicity problems associated with hand builders are:

1. Thermosetting polymers have a tendency to release formaldehyde. Formaldehyde has a limited evidence of a carcinogenic effect, may cause sensitization by skin contact, irritates mucous membranes, causes teary eyes, induces cough and can lead to difficulties in breathing and headaches.
2. Starch derivatives have high BOD and often produce high levels of total suspended solids (TSS), which are difficult to remove or settle (US EPA, 1996).

## 4.3 *Easy-care and durable-press finishes of cellulosics*

The primary effects of easy-care and durable press finishes are the reduction in swelling and shrinkage, improved wet and dry wrinkle recovery, smoothness of appearance after drying, and retention of intentional creases and pleats.
Easy-care and durable press finishes are applied to cellulose fabrics and fabric blends with high cellulose content that are laundered and which should maintain a smooth appearance through the lifetime of the article. These include shirts, blouses, trousers, work clothes, lining fabrics, suits, formal wear and overcoats.
Main easy-care and durable press finishers used in the textile industry are indicated in Table 6.

**Table 6. Easy-care and durable press finishes**

| Chemicals | Subgroup |
|---|---|
| Dimethylether of DMU (dimethylol urea) (U/F)<br>Trimethylol melamine (TMM) (M/F)<br>Hexamethylol melamine (HMM) (M/F)<br>1,3-Dimethylol-4,5-dihydroxyethylene urea (DMDHEU) (U/glyoxal/F)<br>Ether-modified DMDHEU<br>DMDHE + diethylene glycol (Ultra Low Formaldehyde release) | Formaldehyde containing products |
| N,N'-Dimethyl-4,5-dihydroxyethylene urea (DMeDHEU) | Non-formaldehyde containing products |

The main ecological and toxicity problems associated with several easy-care and durable-press finishes are the following ones:

1. Urea/formaldehyde (U/F) containing products have high content and release of formaldehyde.
2. Melamine/formaldehyde (M/F) containing products have relatively high formaldehyde content and release.

## 4.4 *Repellent finishes*

Finishes that repel water, oil and dry dirt are important in all parts of textile market. Water repellency is achieved using different product groups, but oil repellency is attained only with fluorocarbon polymers. Typical textile applications for repellent fabrics are in sport and leisure wear, uniforms, workwear, upholstery and automotive fabrics, awnings, sunblinds, curtain fabrics, table and bed linen, and carpets. Main repellent finishers used in the textile industry are indicated in Table 7.

**Table 7. Repellent finishes**

| Chemicals | Subgroup |
|---|---|
| Emulsions that contain aluminium or zirconium salts of fatty acids, usually stearic acid | Paraffinic repellents |
| Compounds formed by reacting stearic acid and formaldehyde with melamine | Stearic-and-melamine repellents |
| Polydimethylsiloxane products<br>Silanol + silane + tin octoate | Silicone-water repellents |
| Perfluoro alkyl groups incorporated into acrylic or urethane monomers<br>Fluorocarbon polymers applied together with dendrimers | Fluorocarbon-based repellents (FC) |

The main ecological and toxicity problems associated with several repellent finishes are the following ones:

1. Stearic acid-melamine repellents have a tendency to release formaldehyde.

2. The waste water, especially the residual baths, from silicon-water repellents finishing application processes are toxic to fish.
3. The exhaust air of the drying and curing processes of fluorocarbon finishes often contains high amounts of volatile organic compounds (VOC), like glycols and other organic solvents, and a lower content of residual monomers.
4. There is a need for special treatment of waste water from fluorocarbon-based repellents application processes.
5. Possible residual content of perfluoro-octane sulphonate (PFOS) and perfluoro-octanoic acid (PFOA) in fluorocarbon polymers. Both compounds are moderately toxic to mammals, bioaccumulative and very persistent to abiotic and biotic degradation (Kärrman et al., 2007; Trudel et al, 2008; Negri et al., 2008; Jogsten et al., 2009). According to information from trade associations neither PFOS nor PFOA are used in the main production method today, telomerisation, and the substances do not occur either as by-products or end products in this process (BfR, 2007). However, significant levels of PFOS and PFOA in house dust domestic objects, such as carpets, upholstery and clothes, have been found (Strynar and Lindstrom, 2008; Trudel et al., 2008; Fromme et al., 2009b; Guo et al., 2009). Hand-to-mouth transfer from treated carpets seems to be an important exposure route to perfluorinated compounds (PFC), especially in children from North America and Europe (Trudel et al., 2008).

## 4.5 *Soil-release finishes*

Soil-release finishes on textiles facilitate the removal of soils during laundering under common household conditions. The performance of a soil-release finish depends upon its ability to provide a hydrophilic surface during laundering process. Typical textile applications for soil-release fabrics are in active and leisure wear, industrial uniforms and napery (tablecloths and napkins). Main soil-release finishers used in the textile industry are indicated in

Table 8.

**Table 8. Soil-release finishes**

| Chemicals | Subgroup |
|---|---|
| Acrylic and methacrylic acid and ester copolymers<br>Styren-maleic anhydride copolymers<br>Sodium carboxymethyl cellulose (Na-CMC) | Carboxy-based |
| Starch<br>Methyl cellulose<br>Ethyl cellulose<br>Hydroxypropyl starch<br>Hydroxyethyl cellulose<br>Hydroxypropylmethyl cellulose<br>Hydrolysed cellulose acetates | Hydroxy-based (applied in combination with a binder or crosslinking agent) |
| Condensation copolymers of terephthalic acid with ethylene glycol and polyethylene glycol (for polyester fibres) | Ethoxy-based |
| Hybrid hydrocarbon of the block copolymer type | Fluorine-based |
| Alkali and plasma treatments (more hydrophilic fibre surface) | Non-polymer |

No relevant ecological and toxicity problems associated with non-slip finishes have been identified.

## 4.6 *Flame-retardant finishes*

Flame-retardant finishes are applied on firefighters and emergency personnel garments and on floor coverings, upholstery and drapery, especially when used in public buildings. In the UK nightwear and mattresses for children are often given a flame-retardant finish too (BfR, 2007). However, according to BfR no flame retardants should be applied to textiles for private use, or at the very least, products of this kind should be labelled accordingly (BfR, 2007). A flame-retardant finishing may account for up to 20% of product weight. Main flame-retardant finishers used in the textile industry are indicated in

Table 9.

**Table 9. Flame-retardant finishes**

| Chemicals | Subgroup |
|---|---|
| Diammonium phosphate<br>Ammonium sulfamate<br>Ammonium bromide<br>Ammonium polyphosphate | Non-durable flame retardants for cellulose |
| Tetrakis(hydroxymethyl)phosphonium chloride (THPC) + urea<br>N-methylol dimethylphosphonopropionamide + trimethylol melamine + phosphoric acid | Durable flame retardants for cellulose |
| Alkyl dioxaphosphorinane disulfide | Flame retardants for rayon |
| Hexafluoro zirconate and titanate salts<br>Tetrabromophthalic anhydride (TBPA) | Flame retardants for wool |
| Trisdibromopropylphosphate (Tris)<br>A mixture of cyclic phosphate/phosphonates<br>Hexabromocyclododecane (HBCD) | Flame retardants for polyester |
| Phosphorous- and bromine-containing compounds<br>Condensation product of thiourea + formaldehyde + urea<br>Antimony trioxide + decabromodiphenyl ether (DecaBDE) + binder (back-coating of nylon carpets) | Flame retardants for nylon |

The main ecological and toxicity problems associated with several flame-retardant finishes are the folowing:

1. TBPA is suspected to generate polybrominated dioxins under burning conditions.
2. Tris was shown to be a potential carcinogen and was eventually removed from the marketplace.
3. Dust may contain antimony oxide.
4. Formaldehyde release during curing of the permanent flame retardant finishes of cellulose and free formaldehyde of finished fabrics (storage, transport).
5. Phosphorous, antimony and zirconium compounds and halogenated organic flame retardants, especially aromatic ones, in waste water may impose harm on the environment.

6. Halogenated compounds, especially aromatics, are capable of generating polyhalogenated dioxins and furans, and whether or not, hexa- and deca-bromium compounds (HBCD or DecaBDE) are more dangerous.
7. DecaBDE belongs to the category of the polybrominated diphenyl ethers (PBDEs), which are persistent organic polutants (POPs), so they persist in the environment and bioaccumulate in organisms. They also have the potential to disrupt thyroid hormone balance and contribute to a variety of developmental deficits. PBDEs may also have the potential to cause cancer (Illinois EPA, 2006).

There is a huge amount of literature about the environmental concerns associated with brominated flame retardants (de Wit, 2002; Birnbaum and Staskal, 2004; Law et al., 2006), and in particular with PBDEs (Law et al., 2003; Voorspoels et al., 2003; Domingo et al., 2008; Fromme et al., 2009a; Blocksom et al., 2010; Schecter et al., 2009; Letcher et al., in press).

## 4.7 *Non-slip finishes*

The main effect of non-slip finishes is to increase the adhesion between fibres and yarns regardless of fabric construction. Lining and pocketing fabrics made of smooth synthetic filaments are finished with friction enhancers, among others; umbrella fabrics made from nylon or polyester filament yarns are also treated with friction enhancers. Main non-slip finishers used in the textile industry are indicated in Table 10.

**Table 10. Non-slip finishes**

| Chemicals |
|---|
| Dispersions of silicic acid |
| Dispersions of aluminium oxide |
| Polymeric film formers (copolymers of vinyl, acrylic and methacrylic monomers) |

No relevant ecological and toxicity problems associated with non-slip finishes have been identified.

## 4.8 *Antistatic finishes*

Antistatic finishes are applied to all synthetic fibres very shortly after their exit from the spinnerets, but then they are usually removed during fabric preparation. Textiles that are treated with non-durable antistatic finishes include carpets for computer rooms, upholstery fabrics and airbags for automobiles, conveyor belts, filtration fabrics, airmail bags, parachutes, fabrics for hospital operating rooms, and protective clothing for work with flammable gases, liquids and powdered solids. Most of these textile articles are neither washed nor shampooed. Main antistatic finishers used in the textile industry are indicated in Table 11.

**Table 11. Antistatic finishes**

| Chemicals | Subgroup |
|---|---|
| Esters of phosphoric acid<br>Ditallowdimethylammonium chloride<br>Dihydrogenated tallowdimethylammonium chloride<br>Ethoxylated fatty esters, alcohols and alkylamines<br>Mixtures of cationic and non-ionic surfactants | Non-durable finishes |
| Crosslinked polyamines and polyglycols<br>Polyhydroxypolyamines<br>Polyalkylene and polyacrylic copolymers | Durable finishes |
| Dispersing carbon particles or other antistatic agents in polymer melts prior to extrusion<br>Depositing carbon or metallic coatings onto fibre surfaces | Conductive fibres |

No relevant ecological and toxicity problems associated with antistatic finishes have been identified.

## 4.9 *Anti-pilling finishes*

Pills are masses of tangled fibres that appear on fabric surfaces during wear or laundering. There is no group of anti-pilling products in the International Textile Auxiliaries Buyers' Guide (Schindler and Hauser, 2004); a variety of reasons explains this fact: a large variety of parameters influence the pilling behaviour, products primarily used for other purposes are mostly recommended for anti-pilling finishes, etc. Fabrics made from cotton, wool or rayon do not usually dis-

play pilling problems but pilling can be particularly severe in the case of fibre blends. Thus, articles made from cotton and polyester fibres or from any synthetic fibre with wool benefit from an anti-pilling treatment. Main anti-pilling finishers used in the textile industry are indicated in Table 12.

**Table 12. Anti-pilling finishes**

| Chemicals |
|---|
| Polymeric coating (acrylic copolymers) + lubricants |
| Pilling-poor fibres (reduce fibre strength) |
| Cellulase enzymes (100% cotton fabrics) |

No relevant ecological and toxicity problems associated with non-slip finishes have been found.

## 4.10 *Elastomeric finishes*

Elastomeric finishes are also referred to as stretch or elastic finishes and are particularly important for knitwear. These finishes are currently achieved only with silicone-based products. An alternative approach to providing fabrics with elastomeric finishes is to incorporate a few percent of elastic fibres (mostly segmented polyurethanes) into the yarn making process prior to fabric manufacture. Elastomeric finishes are used with swimwear, lingerie, foundation garments, athletic wear, hosiery and normal clothing. Main elastomeric finishers used in the textile industry are indicated in Table 13.

**Table 13. Elastomeric finishes**

| Chemicals |
|---|
| Silanol+ methyl hydrogen silane + metal salt catalyst (Tin octoate) |
| Epoxy-modified silicones (reactive fixation) |

Ecological and toxicity problems associated with elastomeric finishes are related to the handling of epoxides. They need special care since they are potentially physiologically dangerous.

## 4.11 *Finishes to improve colour fastness*

Colour fastness is the resistance of a material to change in any of its colour characteristics, to the transfer of its colorants to adjacent materials or both. Fading means that the colour changes and lightens. Bleeding is the transfer of colour to a secondary, accompanying fibre material. The main finishers being used in the textile industry to improve colour fastness are indicated in Table 14.

**Table 14. Finishes to improve colour fastness**

| Chemicals | Associated dyes or fibres | Subgroup |
|---|---|---|
| Polyacrilic acid derivatives<br>Peroxidases | For removing reactive dyes hydrolysates | |
| Polyquats -polyammonium compounds (polydiallyldimethyl ammonium chloride (DADMAC)) | For direct or reactive dyed cellulose | |
| Formaldehyde condensation products from urea/melamine | For lining fabrics | Improved wet fastness |
| Condensation products of aromatic sulfonic acids (Syntan) | For nylon fibres | |
| Epoxy derivatives with cationic structures (reactive fixation compounds) | For cellulose fibres | |
| Benziphenone<br>Benzotriazol<br>Phenyl triazine<br>□-Cyano-acrylic acid derivatives<br>Titanium dioxide | | Improved light fastness (interaction with light (UV light absorbers) |
| Copper complexes<br>Sodium phosphorous<br>Molybdenum tungstenate<br>Hindered phenol light stabilisers (HPLS)<br>Hindered amine light stabilisers (HALS) | | Improved light fastness (Interaction with the dyestuff) |
| Partially hydrolysed polyvinylacetate (PVAc/PVA) or polyvinylether<br>Pigment binders based on acrylic copolymers | | Improved crocking or rubbing fastness |

Ecological and toxicity problems associated with several finishes used to improve colour fastness are the following ones:

1. For peroxidases, the potential toxicity of the resulting aromatic nitro-compounds (cleavage products of the reactive azoic dyes) has to be resolved.
2. Cationic products (e.g. DADMAC) can cause fish toxicity and are almost non biodegradable.
3. The high reactivity of the reactive fixation compounds may cause cancer or mutagenicity when they come into contact with the finish workers.

## 4.12 *UV protection finishes*

UV protection finishers must prevent fabrics from harmful effects of solar ultraviolet radiation on human skin. Lightweight woven and knitted fabrics intended for producing shirts, blouses, T-shirts, swimwear, beachwear, sportswear, awnings, canopies, tents and blinds benefit from a UV-protective treatment. Main UV protection finishers used in the textile industry are indicated in Table 15.

**Table 15. UV protection finishes**

| Chemicals | Subgroup |
|---|---|
| Phenyl salicylates<br>Benzophenones<br>Benzotriazoles<br>Cyanoacrylates<br>Phenyltriazines | For synthetic fibres |
| Benzotriazole derivatives<br>Oxalic acid dianilide derivatives | For natural fibres |

No relevant ecological and toxicity problems associated with non-slip finishes have been identified.

## 4.13 *Antimicrobial finishes*

Two different aspects of antimicrobial protection provided by chemical finishes can be distinguished: protection of the textile user against pathogenic or odour

causing microorganisms, and protection of the textile itself from damage caused by mould, mildew or rot producing microorganisms.

Antimicrobial finishes (biocides) are particularly important for industrial fabrics that are exposed to weather. Fabrics used for awnings, screens, tents, tarpaulins, ropes, and the like, need protection from rotting and mildew. Carpeting, shower curtains, mattress ticking, upholstery, and intimate apparel also frequently receive antimicrobial finishes.

Main antimicrobial finishers used in the textile industry are indicated in Table 16.

**Table 16. Antimicrobial finishes**

| Chemicals | Subgroup |
|---|---|
| Tributyl tin oxide (TBTO) (deleted in many countries)<br>Dichlorophene<br>3-Iodopropynylbutyl carbamate<br>Benzimidazol derivatives<br>Triclosan<br>Salicylanilides<br>Alkylolamide salts of undecylenic acid<br>Organo-silver compounds and silver zeolites<br>Organic nitro compounds incorporated into the fibre | Antimicrobials for controlled release |
| Octadecylaminodemethyltrimethoxysilylpropylammonium chloride<br>Polyhexamethylene biguadine (PHMB)<br>Chloramines into the fibre<br>Chitosan | Bound antimicrobials |

Ecological and toxicity problems associated with several antimicrobial finishes are the following ones:

1. Some consumers may develop dermatitis from prolonged skin contact with antimicrobial finishes.
2. If residual finish is improperly disposed of at the finishing plant, the desirable and necessary microbes in the waste treatment facility can be destroyed, causing serious ecological problems.
3. Triclosan has a wide application range in the textile sector but it is recalcitrant in nature and has high AOX content (Arslan-Alaton, 2007).

## 4.14 *Insect resist and mite protection finishes*

Insect resist finishes, including protection against dust mites, are chemical treatments that protect wool and other animal fibres from attack by larvae of certain moths and beetles. The most important market for insect resist finishes is the carpet industry. Other significant markets include home furnishing and upholstery fabrics, blankets, uniforms, apparel and furs. Main repellent finishers used in the textile industry are indicated in Table 17.

**Table 17. Insect resist and mite protection finishes**

| Chemicals | Subgroup |
|---|---|
| Chlorinated triphenylmethanes<br>Chlorphenylids<br>Sulcofenurons<br>Flucofenurons | Digestive poisons |
| Dieldrin (banned in most countries)<br>Permethrin<br>Hexahydropyrimidine | Nerve poisons |

Ecological and toxicity problems associated with several insect resist and mite protection finishes are those typical of pesticides. However, it is worthy to note that digestive poisons present a lower environmental hazard than nerve poisons.

## 4.15 *Dyestuffs*

World production of colorants is circa 1 million tonnes per year, of which circa 50% are textile dyes (Nousiainen, 1997). Textiles may be dyed in fibre form (before spinning), as spun yarns, after the finished material has been woven or knitted into textile fabric or, in the case of apparel, in garment form after cutting and sewing. Printing differs from dyeing in that the colour is applied only to specific areas, instead of colouring the whole fabric.

Textile dyes may be classified by their solubility, chemistry or dyeing process used. When classification is based on solubility, a distinction is made between

two groups: dyes, which are deemed to be soluble in the application medium, and not readily or insoluble pigments. It is assumed that pigments are not absorbed through the skin as long as they are not readily soluble (solubility < 1 mg/l).

When classification is by colouring groups (chromophores), i.e. from the chemical angle, a distinction is made between azo dyes, anthroquinone dyes, metal complex dyes and others (BfR, 2007). They can also be classified by usage or application. Table 18 gives some information about the most important dyes.

**Table 18. Main dye classes and characteristics**

| Dye class | Description | |
|---|---|---|
| Acid | Fibres | Nylon, wool, silk, some modified acrylic textiles |
| | Characteristics | Water-soluble<br>Anionic compounds<br>Acidic medium<br>Bright colours<br>Good to excellent fastness properties |
| | Dye-fibre affinity | Ionic bounds between sulfonic acid part of the dye and the basic amino groups in wool, silk and nylon fibres |
| | Environmental concerns | Environmental concerns surrounding mordants (Cr, Sn, Cu, Al), which can be used to improve wet fastness and perspiration fastness of acid dyes, have to be taken into consideration |
| Naphtol (azoic dyes developed on the fibre) | Fibres | Cotton, rayon, cellulose acetate, linen, jute, hemp, sometimes polyester |
| | Characteristics | Coupling (derived from beta-naphtol, available in powder or liquid form) and diazo components (available as free bases and diazonium salts)<br>Good light fastness<br>Good fastness to peroxide and other bleaches |
| | Dye-fibre affinity | Azoic dyes are made up of two chemically reactive compounds. The reaction of the two compounds in the fibre produce the coloured azo chromophore |
| | Environmental concerns | Use has declined over the years because of concerns about the possible presence of carcinogenic naphthylamines in the effluent |
| Basic (cationic) | Fibres | Silk and wool (using a mordant), synthetic fibres (acrylic, modacrylic, modified nylons and polyesters) |
| | Characteristics | Limited water solubility<br>Applied in weakly acidic dye-baths<br>Brightest dyes available |

| Dye class | Description | |
|---|---|---|
| | | Unlimited colour range |
| | | Poor fastness properties on silk and wool |
| | | Acceptable fastness properties on synthetic fibres |
| | | Exhaust nearly 100% when applied properly |
| | Dye-fibre affinity | Ionic bonds are formed between the cation in the dye and the anionic site on the fibre |
| | Environmental concerns | Exhibit high aquatic toxicity |
| Direct | Fibres | Cotton, rayon, linen, jute, hemp, silk, nylon fibres, mixtures of fibres and leather |
| | Characteristics | Water-soluble |
| | | Anionic compounds |
| | | They can be applied directly to cellulosics without mordants |
| | | Fixatives, which react with the dye, are generally added to hold the dye molecules in place and improve colour fastness |
| | | They yield bright, deep colours |
| | | They vary greatly in light fastness |
| | | Limited wash fastness and ability to withstand exposure to moisture, unless the fabric is after-treated |
| | | Commonly applied for upholstery and drapery fabrics |
| | Dye-fibre affinity | Dyes are absorbed into hydrophilic fibres as the fibres expand in the water solution. The dye molecules are held in place through Van der Waals forces and hydrogen bonds |
| | Environmental concerns | Beneficial from a pollution prevention standpoint because they use low amounts of salt and other offensive materials |
| Disperse | Fibres | Polyester and other synthetics (oleophylic fibres), cellulose acetate nylon (i.e. regenerated cellulose fibres), nylon, acrylic fibres |
| | Characteristics | Very low water solubility |
| | | Applied as a dispersion of finely ground powders in the dye-bath |
| | | High temperature and super-atmospheric pressures are sometimes used for application |
| | | Limited build-up properties |
| | | Poor wash fastness in dark shades |
| | | Mostly used to obtain pastel shades in nylons and acrylics |
| | | Good fastness to light, perspiration, laundering and dry cleaning |
| | | Good cracking resistance |
| | Dye-fibre affinity | They transfer into the synthetic fibre polymer because of their high solubility in the substrate |
| | Environmental concerns | No relevant ecological problems associated with disperse dyes have been found |
| Fibre | Fibres | Cellulosic fibres (cotton, rayon), wool, silk, nylon, leather |

| Dye class | Description | |
|---|---|---|
| reactive | Characteristics | Water-soluble<br>Anionic compounds<br>High wet fastness<br>Largest dye class in commercial value<br>Bright shades available<br>Excellent fastness<br>Large amounts of salt are generally necessary, and substantial amounts of dye can remain unfixed at the end of the process (an anionic surfactant is necessary to remove the unreacted dye)<br>Bifunctional reactive dyes increase the efficiency of dye fixation |
| | Dye-fibre affinity | They form covalent chemical bonds with the fibre and become part of the fibre |
| | Environmental concerns | The relatively low fixation efficiency of the dyes results in effluent colour, which is not easily removed<br>Large amounts of salt are necessary |
| Mordant (chelating agent) | Fibres | Wool, silk, nylon |
| | Characteristics | Fair to good fastness properties<br>The shade of dyeing depends on the type of metallic mordant used |
| | Dye-fibre affinity | The fibre is first treated with a metal and the metal exchanged fibre (mordanted fibre) is contacted with a solution containing a complexing agent, typically a chelating agent, called mordant dye. The reaction between the ligand and the exchanged metal forms a metal-chelate complex on the surface of the fibre, which is immobilized. |
| | Environmental concerns | Concern about toxic metal salts in the effluent: metal extraction into the ligand solution during the chelation process (resulting in metal loss from the fibre) and loss of ligand in the solution to the waste stream (loss of expensive ligand and pollution concerns)<br>The metals, ligands, as well as the metal-ligand complexes are present in the waste streams necessitating costly water treatment processes |
| Pigment | Fibres | Pigment dyeing offer the advantages of universal applicability to all fibres |
| | Characteristics | Commonly used for heavy textiles (e.g. canvas), dress materials, shirting, bed linen and furnishing articles<br>Remain insoluble during application<br>Have no affinity for the fibres<br>Require binders<br>Do not react with the fibres |
| | Dye-fibre affinity | Pigments are usually mixed with a binder (aqueous dispersion of cross-linkable mixed polymers) that hardens upon drying, forming an opaque coating |
| | Environmental | In pigment printing the printing paste can be main sources |

| Dye class | Description | |
|---|---|---|
| | concerns | of formaldehyde |
| Sulphur | Fibres | Cotton, rayon, blends of cellulosic and synthetic fibres (nylon, polyester) |
| | Characteristics | Very bleach fast to oxidizing bleaches (e.g. peroxide)<br>Excellent wash fastness<br>Moderate to low light fastness<br>They encompass a broad shade range, but they are mostly used for dark shades<br>Dull compared with other classes |
| | Dye-fibre affinity | Sulphur dyes are reduced to a water-soluble form before application to the fibre and then they colour by absorption.<br>The reducing agent in the dyeing of textile material with sulphur dyes is sodium hydrosulphite, which is used in combination with glucose, although in some cases sulphur dyes are still being reduced using sulphides ($Na_2S$, NaHS) and polysulphides ($Na_2S_8$) |
| | Environmental concerns | Sulphide residues cause environmental concerns (see vat dyes) |
| Vat | Fibres | Cotton, cellulosic fibres |
| | Characteristics | Excellent fastness properties<br>Good range of colours<br>Shade ranges are generally dull<br>Preparation, including bleaching and mercerizing, is important<br>Insoluble in water but soluble in alkaline solution<br>Commonly applied to towels, industrial and military uniforms, and tents |
| | Dye-fibre affinity | They are either supplied in water soluble reduced leuco form or reduced with a reducing agent (e.g. sodium hydrosulphite). Then they are allowed to migrate into the fibre. When this migration is complete, the substrate is rinsed to remove surface dye, then the dye is oxidized back to its water insoluble form within the fibre |
| | Environmental concerns | Sodium hydrosulphite is finally oxidised into compounds (sodium sulphate ($Na_2SO_4$), sulphite ions ($SO_3^{2-}$) and thiosulphate ions ($S_2O_3^{2-}$)) whose release affect the environment detrimentally due to their toxicity<br>The wastewater may contain considerable excess of sodium hydrosulphite ($Na_2S_2O_4$), which is classified in some countries among the most hazardous class of waters<br>The formed sulphate deposits can form toxic hydrogen sulphide ions ($HS^-$) by anaerobic degradation (Bozic & Kokol, 2008) |

Several acute (short-term) and chronic (long-term) toxicological problems have been associated with dyes. Short-term problems include oral ingestion and in-

halation, skin and eye irritation, and skin sensitisation; the main long-term effect of textile dyes is carcinogenicity (cancer-causing).

Short-term problems can arise with polyester, polyamide or acetate rayon dyed with disperse dyes, which have a sensitising potential since the low sweat-fastness allows the dyes to migrate to the skin (Gregory, 2007).
There is evidence that some reactive dyes cause allergic reactions in textile workers (Hunger, 2003; Gregory, 2007). However, no cases of allergic reactions have been reported by consumers wearing textiles dyed with reactive dyes (Hunger, 2003) since the reactive group is no longer present after dyeing and fixation.
Genotoxicity problems of dyes became apparent during the period 1930-1960, when a high incidence of bladder cancer was observed in plant workers. Specific compounds involved were fuchsine, auramine, benzidine and 2-naphthylamine. Nowadays, virtually all dye companies have ceased production of these compounds (Hunger, 2003). In textile dyes the carcinogen component may be the dye itself or a metabolite of the dye. For instance, several azo dyes are likely to cleave into carcinogenic aromatic amines upon reduction of the azo dye.

# 5 Possible substances to be assessed

According to the work scheme planned in agreement with WP5 partners, after the identification of the chemical additives used in the textile sector (task 1), a first selection of the most interesting substances was done (task 2-3). These were the substances considered as potential candidates:

- **Flame retardants**: brominated flame retardants (e.g. HBCD). These substances have been appointed by more than one of the partners as interesting chemicals to be studied in detail. The reason to choose HBCD rather than PBDEs is due to the fact that WP7 is already studying these chemicals as additives in electronics.

- **Repellent finishers**: perfluorocarbon compounds (PFOS and PFOA). These compounds are persistent organic pollutants used increasingly as surfactants in many industries such as textile.
- **Antimicrobial finishers (biocides):** antimicrobials for controlled release (e.g. Triclosan). UCSC showed great interest in the research on these chemicals and their properties since antimicrobial and antifungal agents are of great importance when talking about health issues.
- **Easy-care and durable press finishers**: formaldehyde-containing products (e.g. TMM and HMM). Formaldehyde is present in many different textile products. Systemic or local allergic reactions attributed to it have been reported in many studies, from here the importance of its study.
- **Dyestuff**: mordants (metals). Metals such as Pb, Hg are already studied in WP7 as additives in electronics. However, the use of metals (in particular, chromium) in the process of textile dyeing and their potential damage to the environment, together with their toxicity for human health, make them candidates to be included in the final study.

After a period of discussion among WP5 partners, three substances were selected for a deep study: flame retardants (HBCD), repellent finishers (Perfluorocarbon compounds) and biocides (USCS).
In the following sections, risk scenarios for these three substances are presented.

# 6 Perfluorocarbon Compounds

## 6.1 *Introduction*

Perfluorinated substances are characteristic to contain a total fluorinated carbon chain (hydrogen atoms are substituted by fluorine atoms). This contributes to the perfluorinated compounds (PFC) stability, because the electro negativity of fluorine, C-F bound is one of the largest energy bound.

Perfluorocarboxilic acids (PFCA) are fully fluorinated carboxylic acid. PFCA are named according the chain length, for example, perfluorononanoic acid (PFNA) for 9 C, perfluorodecanoic acid (PFDA) for 10C, and so on. One on the most studied was perfluorooctanoic acid (PFOA) due this similarity with per fluorooctanoic sulfonate (PFOS). In May 2009, PFOS was added to Annex B of the Stockholm Convention on Persistent Organic Pollutants. PFOS is extremely persistent, bioaccumulative and toxic.

Perfluorooctanoic acid (PFOA), also called “C8” is a synthetic chemical and fluorosurfactant. Companies use PFOA to make fluoropolymers, substances with special properties that have thousands of important manufacturing and industrial applications, such as aerospace, automotive, building/construction, chemical processing, electronics, semiconductors, and textile industries. Fluoropolymers confer valuable properties, including fire resistance and oil and water repellence. They are used to provide non-stick surfaces in waterproof and breathable membranes kitchenware, for clothing.

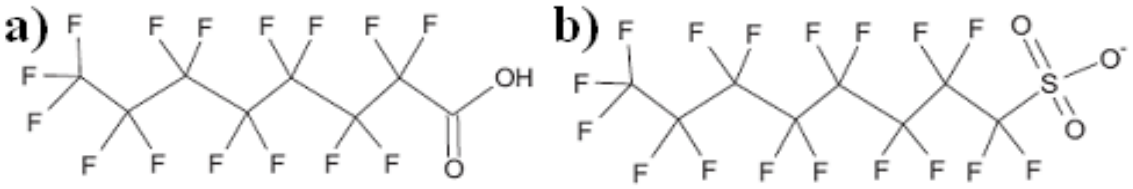


***Figure 3. Perfluorooctanoic acid (PFOA)(a) and Perfluorooctanoicsulfate (PFOS)(b).***

## 6.2 *Environmental Sources*

- Direct Sources: Manufacturing and use of PFOA are the main emission sources to air and water. While manufacturing of PFOA or their derivates (polymer/telomers) are focalized in a few factories in the world, the final applications of PFOA derivates to the product (textile and clothing) are very diffuse.
- Indirect Sources: There are two different kinds,
    - Impurities of material, PFOA-derivates may contain trace of PFOA

- Degradation, during the use of consumer product or during the end of life product (disposal on the landfill or incineration).

Figure 4 shows the estimated historical of perfluorooctanoate (PFO) emissions from 1950 to 2004, as well as the future trends (2005-2050). The results were very similar to those obtained by Prevedouros et al. (2006) for PFOA (Figure 5).

**TABLE 1. Estimated Historical (1950–2004) and Future (2005–2050) PFO Emissions[a]**

| PFO emission source | 1950–2004 min–max (metric tons) | % of total PFO emission (average) | 2005–2050 min–max (metric tons) | % of total PFO emissions (average) |
|---|---|---|---|---|
| | **Direct Sources** | | | |
| FP manufacturing (APFO) | 2060–4090 | 72.3% | 410–815 | 86.0% |
| APFO manufacturing | 370–590 | 11.8% | 20–40 | 4.2% |
| FP dispersion (APFO) | 215–340 | 6.8% | 45–75 | 8.7% |
| AFFF-ECF | 50–100 | 1.8% | 0 | 0% |
| FP manufacturing (APFN) | 3–10 | 0.1% | <1–2 | 0.1% |
| Consumer & Industrial Products | 2–10 | 0.1% | 0 | 0% |
| APFN manufacturing | 1–2 | 0% | <1 | 0% |
| PVDF (APFN) | <1 | 0% | <1 | 0% |
| Σ *direct sources:* | 2700–5140 | 92.9% | 475–932 | 99.0% |
| | **Indirect Sources** | | | |
| POSF raw material degradation | 4–585 | 5.0% | 0 | 0% |
| POSF impurities | 14–110 | 1.2% | 0 | 0% |
| POSF-AFFFs | 2–23 | 0.2% | 0 | 0% |
| FT raw material degradation | 3–60 | 0.6% | 1–14 | 0.8% |
| FT impurities | <1–17 | 0.1% | <1–4 | 0.2% |
| Σ indirect sources: | 23–795 | 7.1% | 1–18 | 1.0% |
| Σ direct and indirect sources: | 2723–5935 | 100.0% | 476–950 | 100.0% |

[a] AFFF = aqueous film forming foams (also aqueous fire fighting foams); APFN = ammonium perfluorononoate; APFO = ammonium perfluorooctanoate; ECF = electrochemical fluorination, a process used to produce fluorinated chemicals; FP = fluoropolymer; FT = fluorotelomer; POSF = perfluorooctanesulfonyl fluoride; PVDF = polyvinylidene fluoride.

**Figure 4. Estimated Historical and future PFO emissions (from Armitage et al., 2006)**

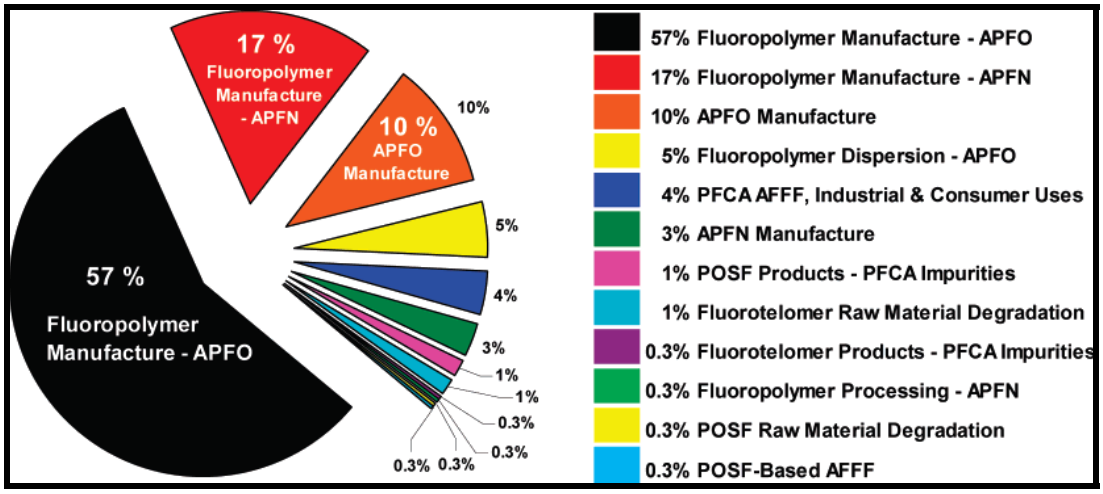


**Figure 5. Percent of total historical global PFCA emissions by source (from Prevedouros et al, 2006).**

Regarding PFCA, the main source of emission of PFCA in the environment is not the production process, but the production of fluoropolymers (Prevedouros et al., 2006). In 2003, there were many fluorpolymers manufacturing sites worldwide. Only in China, there was a total capacity total 240.000 t/y of polytetrafluoroethylene (PTFE) (Chen et al., 2009). The Russian production of fluoropolymers is 100.000 t/y, being about 60–80% of polytetrafluoroethylene (Buznik, 2009).

## 6.3 *Manufacturing and uses of PFOA/PFOS*

PFCA have been manufactured as salts by two main synthesis routes: electrochemical fluorination (ECF) and fluorotelomer iodide oxidation, as shown in Figure 6 (Prevedouros et al., 2006). From 1947 to 2002, EFC was used to manufacture the large part (80-90%) of perfluoroctanoate ammonium salt (APFO). The main production sites were U.S. and Belgium, followed by Italy and, in a smaller scale, Japan. The remaining 10-20% of APFO was produced between 1975 to the current days by oxidation of perfluorooctyl iodide in Germany and Japan.

**Electrochemical Fluorination (ECF).**

$$H(CH_2)_7COF + HF + e^- \rightarrow F(C_2F)_7COF \rightarrow F(C_2F)_7CO_2{\cdot}HH_4$$

Octanoic acidfluoride — **APFO**

**Perfluorooctyl Iodide Oxidation.**

$$F(CF_2)_8I + [O] \rightarrow F(C_2F)_7COOH \rightarrow F(C_2F)_7CO_2{\cdot}HH_4$$

Perfluorooctyl Iodide — **APFO**

**Figure 6. PFCA synthesis routes.**

## 6.4 *PFC world trade*

There are no data on the import or export of PFOS or PFOA available in the statistics of UN and OCDE trade database. However, the trade of polytetrafluoroethylene (PTFE) has been analyzed (Table 19 and Figure 7). The synthesis of PTFE is one of the main uses of PFOA. Fluoropolymers, such as PTFE, are used in non-stick cookware, electronics, textiles, wire and cable coating, semiconductors, etc.

**Table 19. Leading Exporters and importers of Fluoropolymer: polytetrafluoroethylene, 2008. Source: UN Comtrade (2010).**

| Exporter (2008) | Net Weight (t) | % World port | Ex-Importer (2008) | Net Weight (t) | % World Export |
|---|---|---|---|---|---|
| China | 16271 | 18.7 | Italy | 11766 | 14.3 |
| USA | 11432 | 13.1 | USA | 10903 | 13.2 |
| Netherlands | 10128 | 11.6 | China | 6637 | 8.1 |
| Germany | 10070 | 11.6 | Germany | 5873 | 7.1 |
| Italy | 9970 | 11.4 | Rep. of Korea | 5253 | 6.4 |
| Russian Federation | 9110 | 10.5 | Japan | 3604 | 4.4 |
| Japan | 4383 | 5.0 | France | 3430 | 4.2 |
| United Kingdom | 3575 | 4.1 | Netherlands | 3378 | 4.1 |
| China, Hong Kong | 3008 | 3.5 | China, Hong Kong | 3077 | 3.7 |
| Belgium | 2787 | 3.2 | Yemen | 2686 | 3.3 |
| Singapore | 2005 | 2.3 | Belgium | 2482 | 3.0 |
| India | 1904 | 2.2 | United Kingdom | 2446 | 3.0 |
| Romania | 841 | 1.0 | India | 2347 | 2.8 |
| Others | 1688 | 1.9 | Brazil | 2094 | 2.5 |
| | | | Switzerland | 1748 | 2.1 |
| | | | Others | 14668 | 17.8 |
| UN comtrade http://comtrade.un.org/db/default.aspx | | | | | |

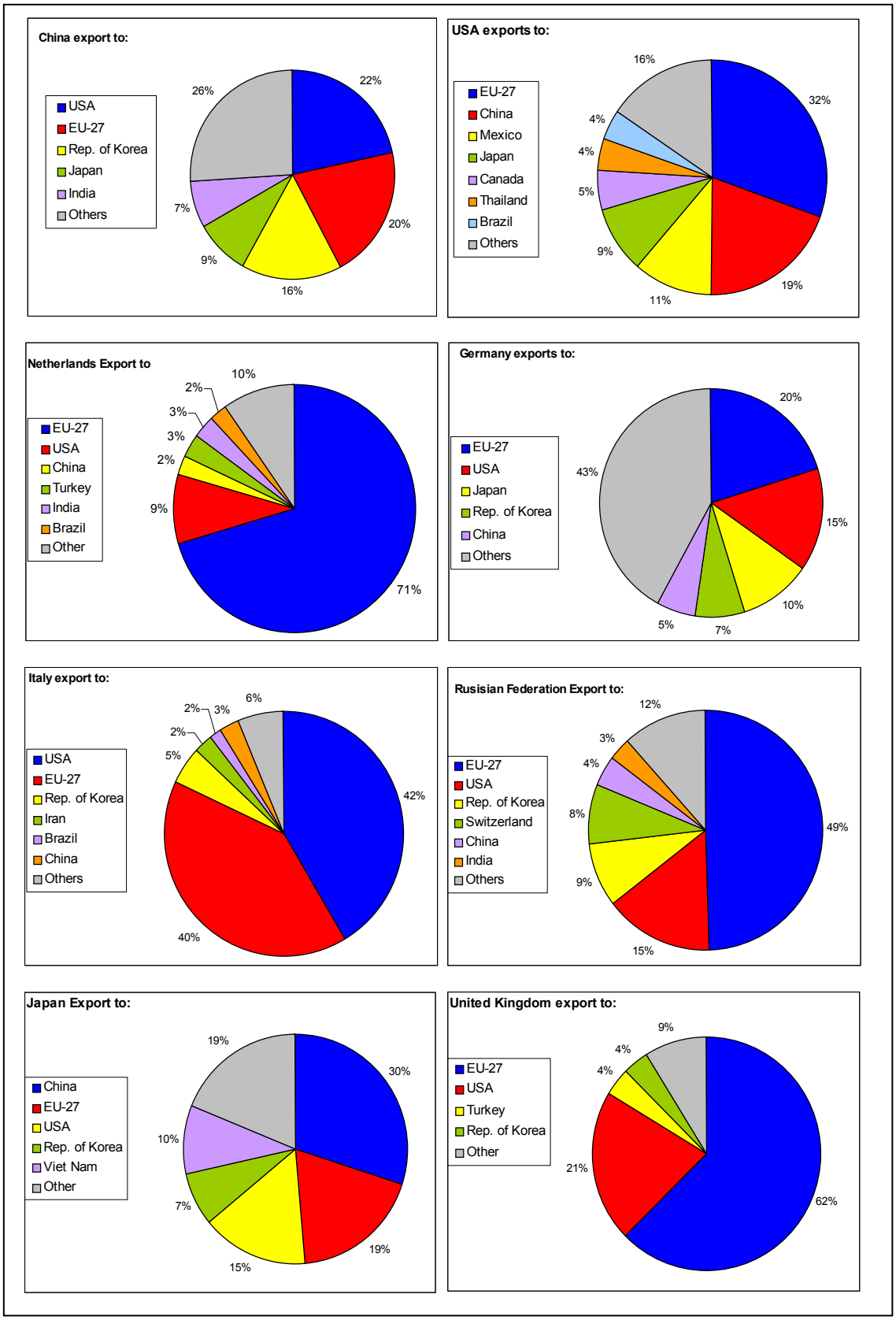


**Figure 7. Destination of Fluoropolymer (% of net weight): Polytetrafluoroethylene exportations of the principals Exporters, 2008. Source UN Comtrade (2010)**

## 6.5 *Consumer products with PFOA and related compounds*

Consumer products made with fluoropolymers and fluorinated telomers may contain trace amounts of PFOA and other related perfluorinated chemicals as impurities. PFOA is also formed by the degradation of precursors such as some fluorotelomers. In a 2009 USEPA study of 116 products -purchased between March 2007 and May 2008-, PFOA concentrations ranged from non-detectable to 6750 ng/g (Table 20).

**Table 20. Concentrations of PFOA in consumers products (Guo et al., 2009)**

| **Product** | **Range (ng PFOA/g Product)** |
|---|---|
| Pre-treated carpeting | ND (<1.5) to 462 |
| Treated apparel | 5.4 to 161 |
| Treated upholstery | 0.6 to 293 |
| Treated home textiles | 3.8 to 438 |
| Treated non-woven medical garments | 46 to 369 |
| Industrial floor wax and wax removers | 7.5 to 44.8 |
| Stone, tile, and wood sealants | 477 to 3720 |
| Membranes for apparel | 0.1 to 2.5 ng/cm$^2$ |
| Food contact paper | ND (<1.5) to 4640 |
| Dental floss/tape | ND (<1.5) to 96.7 |
| Thread sealant tape | ND (<1.5) to 3490 |
| PTFE cookware | ND (<1.5) to 4.3 |

## 6.6 *End-of-life of products containing PFOA*

PFC levels are found in landfill leachates. These levels depend on the type of treatment of leachates, higher levels being leached with biological treatments and wet air oxidation than those treated with activated charcoal and reverse osmosis. The shorter-chain PFCs ($C \leq 6$) were more abundant than longer-chain compounds, whereas the mean contribution of perfluorobutane sulfonate (PFBS) (mean contribution 24%) and perfluorobutanoic acid (PFBA) (27%) represent approximately the half of the ΣPFC proportion (Busch, et al., 2010). A

study of 2 landfills in Denmark (Bossi et al., 2008) showed that landfilling is not a release source of PFCs to the environment.

In addition, Yamada et al. (2005) showed that the polyester/cellulose fabric treated with a fluorotelomer-based acrylic polymer is destroyed and an undetectable amount of PFOA is formed under typical municipal incineration conditions. Therefore, textiles and paper treated with such a fluorotelomer-based acrylic polymer disposed in municipal waste and incinerated are expected to be destroyed and not be a significant source of PFOA in the environment.

## 6.7 *Exposure pathways*

*Occupational exposure*

The highest PFOS and PFOA concentrations in human blood samples have been measured in workers employed in fluorine production plants (Olsen et al., 2003). In most cases, workers occupationally exposed present serum levels of both PFOA and PFOS approximately one order of magnitude higher than those reported in the general population (Lau et al., 2007). Those results pointed out the occupational exposure as the main exposure pathway of both PFOS and PFOA.

*Dietary and dinking water*

Table 21 shows the concentrations of PFOS and PFOA reported in water, according to its origin, found worldwide.

Assuming an intake of 2 L of tap water per day, the daily intake of PFOS and PFOA by the population living in Tarragona County (Catalonia, Spain) was estimated in 0.78-1.74 and 12.6 ng, respectively (Ericson et al., 2008a). On average, for an adult man of 70 kg of body weight, the dietary intake of PFOS in Catalonia was estimated to be 62.5 ng/day (Ericson et al., 2008b). This value is approximately one-half of the PFOS ingestion through drinking water in the worst-case scenario (116.2 ng/day). Among a variety of foodstuffs, PFOA only

could be detected in milk samples. It was concluded that in Catalonia, at least for PFOS, tap water could be a source of exposure to this pollutant even more important than its dietary intake. In turn, Fromme et al. (2009) stated the diet as the main exposure pathway, followed by drinking water and house dust (Figure 8).

**Table 21. Concentration of PFOA and PFOS in water (river, tap and bottled) of recent studies.**

| | n | **PFOS (ng $L^{-1}$)** | **PFOA (ng $L^{-1}$)** | Reference |
|---|---|---|---|---|
| China remote area river | 13 | 0.4 (<0.10-2.4) | 0.1 (<0.10-1.3) | Jin et al., 2009 |
| China Hun River | 11 | 4.9 (0.2-44.6) | <0.10 (<0.10-1.5) | Jin et al., 2009 |
| China Yangtse River | 34 | 4.7 (0.2-37.8) | 5.4 (<0.10-297.5) | Jin et al., 2009 |
| Japan Yodo River | 18 | 2.4 (0.6-49) | 23.8 (4.2-901) | Lein et al., 2008 |
| Japan Yodo River | 30 | 3.8 (0.4-56) | 29.4 (7.4-1044) | Lein et al., 2008 |
| Japan Yodo River | 33 | 5.6 (0.8-123) | 36.6 (6-2568) | Lein et al., 2008 |
| India Ganges northern | 19 | (<0.04-1.81) | (<0.04-0.21) | Yeung et al., 2008 |
| India Ganges southern | 10 | (<0.083-3.91) | (<0.083-23.1) | Yeung et al., 2009 |
| European Rivers (over 100) | >100 | 6 | 3 | Loos et al., 2009 |
| USA/NY State (lakes, rivers, canals) | 51 | (1.6–756) | (15–49) | Sinclair et al., 2006 |
| China Tap water (21 cities) | 21 | 1.8 (<0.1-14.8) | 3.4 (<0.1-45.9) | Jin et al., 2009 |
| Osaka Japan Tap water | 14 | (0.16-22) | (2.3-84) | Takagi et al., 2008 |
| Catalan (Spain) tap water | 40 | 3.7 (<0.1-58) | 4.6 (<0.9-57) | Ericson et al., 2008a |
| Catalan (Spain) bottled water | 4 | <0.2 | (<0.2-0.7) | Ericson et al., 2008a |

Table 9. Estimated adult daily intake of PFOS and PFOA for the general population. Mean intake based on mean or median concentrations; high intake based on upper percentile or maximum concentrations

| | Concentration | | Intake rate [a] | Intake (ng/day) | | Daily intake pg/kg b.w. [b] | |
|---|---|---|---|---|---|---|---|
| | Mean | High | | Mean | High | Mean | High |
| *PFOA* | | | | | | | |
| Indoor air | 4.4 pg/m$^3$ [c] | | 12 m$^3$/day | 0.053 | 0.053 | 0.9 | 0.9 |
| Outdoor air | 58.4 pg/m$^3$ [d] | 552 pg/m$^3$ [d] | 1.3 m$^3$/day | 0.076 | 0.718 | 1.3 | 12.0 |
| House dust | 19.72 ng/g [e] | 1234 ng/g [e] | 50 mg/day | 0.986 | 61.7 | 16.4 | 1028.3 |
| Diet | | | | 169 [h] | 689 [h] | 2816.7 | 11483.3 |
| Drinking water | 1.0 ng/l [f] | 4.0 ng/l [f] | 1.3 l/day | 1.3 | 5.2 | 21.7 | 86.7 |
| Overall intake | | | | | | 2857.0 | 12611.2 |
| *PFOS* | | | | | | | |
| Indoor air | 23.7 pg/m$^3$ [g] | | 12 m$^3$/day | 0.284 | 0.284 | 4.7 | 4.7 |
| Outdoor air | 4.5 pg/m$^3$ [d] | 46 pg/m$^3$ [d] | 1.3 m$^3$/day | 0.006 | 0.060 | 0.1 | 1.0 |
| House dust | 37.8 ng/g [e] | 5065 ng/g [e] | 50 mg/day | 1.9 | 253 | 31.7 | 4216.7 |
| Diet | | | | 90 [h] | 269 [h] | 1500.0 | 4483.3 |
| Drinking water | 1.0 [f] | 6.0 [f] | 1.3 l/day | 1.4 | 7.8 | 23.3 | 130.0 |
| Overall intake | | | | | | 1559.8 | 8835.7 |

**Figure 8. Mean and high daily intake of PFOA for general population (from Fromme et al., 2009).**

*Indoor exposure*

Trudel et al. (2008) calculated the contribution to exposure of several “indoor” pathways (Figure 9). Hand-to-mouth transfer from treated carpets seems to be an important exposure route to PFOA, especially in infants, toddlers and children from North America and Europe. For teens and adults, the migration of PFOA to the papers and cardboards into the food was the main pathway. Food and water ingestion pathway contributed around 15-20% of total exposure in all ages.

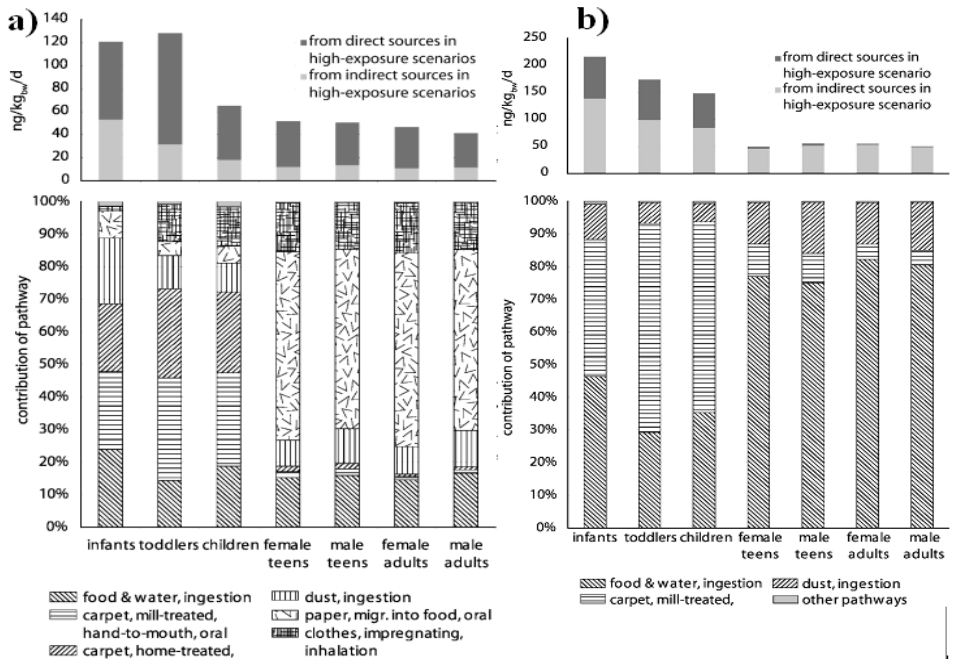


**Figure 9. Direct versus indirect exposure (top) and contribution of pathways (bottom) in North America for the high-exposure scenario to PFOA (a) and PFOS (b) (Trudel et al., 2008)**

## 6.8 *Legislation*

In 2002, the principal APFO worldwide producer by the ECF, 3M, ceased its production. In 2006, US EPA invited the 8 major fluoropolymer and telomere manufacturers to join in a global stewardship program with two goals:

- To commit to achieve, no later than 2010, a 95% reduction, measured from a baseline year 2000, in both facility emissions to all media of PFOA, precursor chemicals that can break down to PFOA, and related higher homologue chemicals, and product content levels of these chemicals.
- To commit to working toward the elimination of these chemicals from emissions and products by 2015.

In 2009, PFOS was included in the list of the Stockholm Convention on Persistent Organic Pollutants (POPs).

The European Union (EU) adopted a resolution of restrictions on marketing and use of PFOS and related substances in 2006. The resolution set the maximum concentrations of 0.1% by mass for PFOS-containing semifinished products or articles, 0.005% by mass for PFOS preparations, and 1 µg/m2 PFOS for textiles or other coated materials. Canada introduced regulations to prohibit production and use of PFOS and its salts and substances that contain one of the following groups: perfluorooctyl sulfonyl (C8F17SO2-), sulfonate (C8F17SO3) or sulfonamide (C8F17SO2N-).

Following the voluntary phase-out of PFOS by the principal worldwide manufacturer, the USEPA introduced a Significant New Use Rule (SNUR) in 2001 on PFOS chemicals, and 3 SNURs on PFAS chemicals in 2002, 2006 and 2007. These SNURs allowed the continuation of a few limited, highly technical uses of these chemicals for which no alternatives were available, and which were characterized by very low volume, low exposure, and low releases. Any other use of these chemicals requires prior notice to and review by the Agency.

## 6.9 *Environmental properties of PFOS/PFOA*

*Fate and transport*

The physicochemical properties of PFOA are summarized in Figure 10 (US EPA, 2005).

| Property | Value |
|---|---|
| Appearance at normal temperature and pressure | White powder/waxy white solid |
| Molecular weight | 414.1 g/mol |
| Vapour Pressure | 0.1 kPa (20 °C)<br>10 mm Hg (25 °C)<br>4.2 Pa (25°C)<br>(APFO: 0.0081 Pa at 20°C) |
| Water solubility in pure water | 3.4 g/L<br>4.1 g/L (22 °C)<br>9.5 g/L (25 °C) |
| Melting point | 45-50 °C |
| Boiling point | 189-192 °C (736 mm Hg) |
| Log $K_{OW}$ | Not measurable<br>(APFO: 0.7; 3M Company, 1979) |
| Log $K_{oc}$ | 2.06 (Higgins and Luthy, 2006) |
| Log $K_D$ | -0.22-0.55 (deVoogt *et al.*, 2006a]);<br>-0.39-0.94 soils (DuPont, 2003a),<br>1.10-1.57 sludge (DuPont, 2003) |
| Air-water partition coefficient | Not available |
| Henry's Law constant | Cannot be estimated [b)] |
| $pK_a$ | 2.5, 2 to 3 (Prevedouros *et al.*, 2006) |

a) As free acid unless otherwise stated

b) The vapour pressure of the pure solid is sufficient to sustain mg/kg concentrations of vapour in the atmosphere, but in practice this is unlikely as PFOA will dissociate in aqueous media thereby reducing its vapour pressure above aqueous solutions. For this reason the Henry's Law constant cannot be estimated from the vapour pressure and solubility.

**Figure 10. Physical-chemical properties of PFOA (from US EPA, 2005).**

The anticipated formation of an emulsified layer between the octanol and water surface interface has made, until now, determination of log $K_{ow}$ impossible. Unlike other POPs, such as PCBs, PCDD/Fs, etc, PFOA has a great potential to dissolve in water.

*Toxicity*

The pharmacokinetic properties of PFOA have been studied in some detail. Animal studies of PFOA exposure have shown that they are well absorbed orally, but poorly eliminated and it is not metabolized. PFOA trends to accumulate in blood, liver and kidneys (Seacat et al., 2002, 2003). Levels of PFOA and other PFCs have also been reported in umbilical cord blood (Inoue et al., 2004).

The half-lives in human blood serum have been estimated to be 3.8 and 5.4 years for PFOA and PFOS (Olsen et al., 2007). The persistence of PFCs in the environment and slow elimination rates in humans means they are likely to accumulate in people. The elimination half-lives of several PFCs are shown in Figure 11 (Lau et al., 2006).

Serum/Plasma Elimination $T_{½}$ of Various PFAAs

| | | PFHS | | | PFBA | | PFOA | | |
|---|---|---|---|---|---|---|---|---|---|
| Species | PFBS | Females | Males | PFOS | Females | Males | Females | Males | References |
| Rat | | | | 100 days | 1.6–1.8 h | 7–9 h | 2–4 h | 4–6 days | Chang *et al.*, 2007a; Johnson *et al.*, 1979b; Kemper and Jepson, 2003 |
| Mouse | | | | | 3 h | 17 h | 17 days | 19 days | Chang *et al.*, 2007a; Lau *et al.*, 2005 |
| Rabbit | | | | | | | 7 h | 5.5 h | Hundley *et al.*, 2006 |
| Dog | | | | | | | 8–13 days | 20–30 days | Hanhijarvi *et al.*, 1982 |
| Monkey | 3.5–4 days | 87 days | 141 days | 150 days | 1.7 days | | 30 days | 21 days | Butenhoff *et al.*, 2004b; Chang *et al.*, 2007a; Lieder *et al.*, 2006b; Noker and Gorman, 2003; Olsen *et al.*, 2005b; Seacat *et al.*, 2002 |
| Human | 1 month | | 8.5 years | 5.4 years | | | 3.8 years | | Olsen *et al.*, 2005a, 2006 |

**Figure 11. Elimination half live of various PFCs in different mammal species (Lau et al., 2006).**

Epidemiologically, no clear correlations have been observed between PFC serum concentrations in human populations and adverse health effects or illnesses (Alexander and Olsen, 2007; Emmett et al., 2006). However, some correlations have been reported with fecundity, as measured by time to pregnancy (TTP) (Olsen et al., 2009), and between PFOA/PFOS and cholesterol levels (Steenland et al., 2009). Others epidemiologic studies have also demonstrated inhibitory effects on human neonatal growth at the background exposure levels of PFOS and /or PFOA in general population (Apelberg et al., 2007; Fei et al., 2007).

For mammalian species, PFOA and its salts have been found to cause cancer in rats and adverse effects on the immune system in mice. In addition, PFOA and its salts can display reproductive or developmental toxicity in rodents at moderate levels of exposure (Lau et al., 2006; OECD, 2006). PFOA is considered a probable human carcinogen by the US Environmental Protection Agency.

# 7 Biocides

## 7.1 *Introduction*

Biocides are defined in the European Directive 98/8/EC as substances that aim at destroying, deterring, preventing the action, or otherwise controlling the effect on any harmful organism by chemical or biological means. In textile industry biocides are used to control bacteria, fungi, mildew, algae and the problems of deterioration, staining, odours, and health concerns that they cause.

Textile fibres can be different according to their origins: natural fibres (cotton, wool, etc…), natural man-made fibres (acetate, rayon, etc…), and synthetic man-made fibres (polyester, poliamide, etc…). In general textiles made from natural fibres are more susceptible to biodeterioration than man-made fibres (Tissier et al., 2001). Animal fibres are susceptible to attack by both micro-organisms and insects, while cellulose fibres (cotton, linen,…) are more sensitive to rot and mildew than animal fibres. Synthetic fibres are hardly subject to deterioration by micro-organisms or insects, however two polymers are more sensitive than others: polyvinyl chloride (PVC) and polyurethanes (PUR). Natural man-made fibres, such as rayon, are readily degraded by mildew and bacteria. Viscose and acetate fibres, both manufactured from natural cellulose, show a different behaviour concerning biodeterioration: viscose fibres are readily degraded by mildew and bacteria whereas acetate is more resistant (Tissier et al., 2001).
Biocides are applied at different steps of the textile production, therefore at each step of their application, releases may occur (Fig. 12) (Tissier et al., 2001):

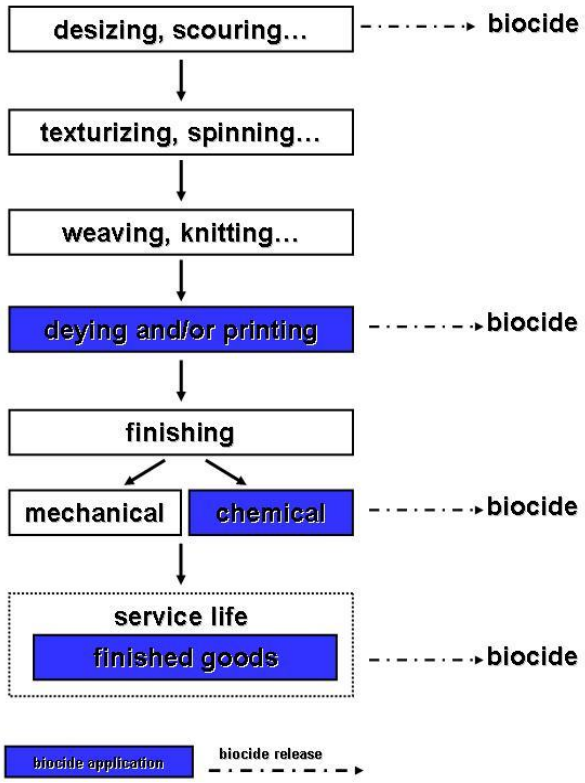


**Figure 32. Applications and releases of biocides in textile industry (from Tissier et al., 2001).**

- imported fabrics: can contain biocides applied for preservation during storage and transport (preservation agents). These biocides are removed by rinsing and released with waste water
- desizing/scouring: this step is one of the largest source of waste water pollutants. Biocides applied during sizing (moth repellents) can be removed in waste water
- dyeing: biocides may be added to dyeing baths

- finishing processes (chemical or mechanical): generate waste water containing natural and synthetic polymers and a range of potentially toxic substances. Biocides are often incorporated with finishing products (e.g. water repellents, fire retardants, etc.)
- finished goods: releases may occur during all life-cycle stages (the final use of textile article, its recycling and disposal)

Therefore, most of the chemicals and additives in textile are released to waste water. Operations that represent the greatest concern are finishing and dyeing.

Usually, fabrics exposed to outdoor conditions (tents, tarpaulins etc.), sanitary products (hospital textiles) and carpets are treated with antimicrobial finishing. Reduction of odour nuisances (e.g. in sportswear) by means of antimicrobial finishing is another typical application field for biocides. Other types of biocides are used as mothproofing agents, for example in the carpet sector to impart wool fibre lifetime protection against a range of textile pests.

The following biocides are typical for the textile industry (OECD, 2004; EC, 2003):

- antimicrobial finishing, such as: isothiazolinone derivatives, triclosan, quaternary ammonium compounds, dichlorophen derivatives, benzimidazole derivatives, tin and zinc organic compounds
- moth proofing, such as: pyrethroids (permethrin, cyfluthrin), sulcofuron derivatives, etc..
- preservation agents for the improvement of the storage stability of textile auxiliaries, such as: chlorinated and non-chlorinated isothiazolinone derivatives, quaternary ammonium compounds, chlorinated benzene, sodium benzoate, etc…

In the present report the attention will be focused on a broad-spectrum antimicrobial biocide, triclosan.

## 7.2 *Triclosan uses*

The application of antimicrobial agents on textiles dates back in the past. Many antimicrobials used for textiles are already known in the foodstuff and cosmetic sectors and have been used for decades (Orhan et al., 2006). Textiles currently used in hospitals and hotels can be conductive to cross infection or transmission of diseases caused by microorganisms, particularly bacteria and fungi. The

major classes of antimicrobials for textiles include organo-metallic phenols, quaternary ammonium salts, organo-silicones, and bis-phenols.
Triclosan (5-chloro-2-(2,4-dichloro-phenoxy)-phenol) (TCS) is a chlorinated aromatic compound, a non-ionic compound, it is used as a synthetic broad-spectrum antimicrobial agent in the form of a white to off-white powder, possessing mostly antibacterial along with some antifungal and antiviral properties (Orhan et al., 2006).

TCS has been used extensively for more than 30 years (Oliveira et al., 2009). It is widely used as an antimicrobial agent in many consumer and professional healthcare products such as soaps, detergents, toothpastes, disinfectants, cosmetics and pharmaceuticals (Ying and Kookana, 2007) and also incorporated into fabrics and plastics (Orhan et al., 2006). In commercial, institutional, and industrial equipment uses, triclosan is incorporated in conveyor belts, fire hoses, dye bath vats, or ice-making equipment as an antimicrobial pesticide. As a material preservative, triclosan is used in many products including adhesives, fabrics, vinyl, plastics (toys, toothbrushes), polyethylene, polyurethane, polypropylene, floor wax emulsions, textiles (footwear, clothing), caulking compounds, sealants, rubber, carpeting, and a wide variety of other products (EPA, 2010).

Due to its widespread use, triclosan featured among the seven most frequently detected compounds in a U.S. survey of 139 streams across 30 states (Kolpin et al., 2002). In Europe, 350 tons of TCS are utilised per year, and approximately 1,500 tons are produced annually worldwide (Singer et al., 2002).

Triclosan is regulated by the Environmental Protection Agency (EPA), the Food and Drug Administration (FDA) and the Consumer Product Safety Commission (CPSC). Europe recently banned triclosan in all items expected to come into contact with food, and has set limits on how much triclosan can be in cosmetics (EC, 2010).

## 7.3 *Physical-chemical properties of triclosan*

Triclosan chemical structure is showed in Figure 13. TCS is hydrolytically stable, relatively non-volatile and is practically insoluble in water, but it is soluble in most organic solvents (Reiss et al., 2002; EPA, 2008) (Table 22).

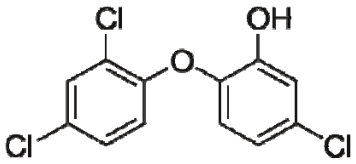


**Figure 13. Triclosan chemical structure**

**Table 22. Physical and chemical properties of triclosan (EPA, 2008; Reiss et al., 2002; SCCS, 2010).**

| Property | Value |
|---|---|
| Chemical name | 2,4,4'-trichloro-2'-hydroxy-diphenylether |
| Chemical name synonyms | Phenol, 5-chloro-2-(2,4-dichlorophenoxy)-; Ether, 2'-hydroxy-2,4,4'-trichlorodiphenyl; 5-Chloro-2-(2,4-dichlorophenoxy)phenol, Trichloro-2'-hydroxydiphenylether |
| Chemical formula | $C_{12}H_7Cl_3O_2$ |
| CAS No | 3380-34-5 |
| Molecular weight | 289.5 |
| Melting point, C° | 57 ± 1 |
| Vapour pressure, Pa | $7 \times 10^{-4}$ (25°C) |
| Water solubility at 20°C, mg/L | 12 |
| Henry's law constant, atm $m^3$ $mol^{-1}$ | $1.5 \times 10^{-7}$ |
| Density, $g/cm^3$ | 1.55 ± 0.04 |
| pKa at 20°C | 8.14 |
| Log $K_{ow}$ | 4.8 |

## 7.4 *Triclosan risk characterization*

All biocides give rise to environmental concern when they are discharged in waste water, because of their toxicity to aquatic life (EC, 2003). Considering that biocides are necessary for the control of organisms that cause damage to natural or manufactured products and that they can pose risks to humans, animals and environment in a variety of ways, the European Directive 98/8/EC

aims at regulate the placing of biocidal products on the market (European Commission, 1998). The scope of the Directive is very wide, covering 23 different product types. The objective of the Biocidal Products Directive is to remove barriers of trade between member states, and at the same time to ensure a harmonised high degree of protection for man and the environment (Rasmussen and MacLellan, 2001) in order to control the risk of biocides at EU level.

For this purpose a registration and admission procedure was developed, based on the risk assessment of biocides. Emission estimations are a prerequisite for this assessment and influence the results of risk assessment to a large extent. According to Annex VI of the Biocidal Products Directive the risk assessment shall cover the proposed normal use of the biocidal product together with a 'realistic worst case scenario'. The methods of estimating the emission rate of "Fibre, leather, rubber and polymerised materials preservatives" to the primary receiving environmental compartments are described. The Directive 98/8/EC include technical detail for conducting hazard identification, dose (concentration) - response (effect) assessment, exposure assessment and risk characterisation in relation to human health and the environment.

### 7.4.1 Environment

Exposure assessment

At each step of application of a biocide, releases may occur in the environment. Imported fabrics can contain biocides applied for preservation during storage and transport to improve textile storage stability (preservation agents). These biocides are removed by rinsing and released with waste water almost completely. Therefore, it is very difficult to know which and how many of these biocides have been applied.

Textile material is submitted to functional finishes. Biocides are often incorporated with finishing products such as water repellents, fire retardants, etc.

Therefore, use of biocides and then their release can occur during the fabric preparation and the finishing processes.

The life-cycle concept means that the emission pathways from all life-cycle stages, including the disposal of the finished product, have to be analysed if relevant emissions occur. Substances, which are intended to fix on the textiles, will be emitted to a great part during disposal. For textiles used under outdoor conditions release of the substances to water and soil is to be considered depending on the water solubility of the substances.

For calculating the releases of a biocide from finishing process the input to be considered should be the degree of fixation of biocides (estimated to be approx. 70-80% (Tissier et al., 2001)), the quantity of fibres/fabrics treated per day, and the quantity of active substance applied per ton of fibres/fabric for the finishing step, as described in OECD (2004) and Tissier et al. (2001).

The widespread use of TCS provide a number of pathways for the chemical to enter the environment. In general releases occur to air, waste water and soil. In the textile industry, air emissions are considered to be negligible pathway, due to the high attachment characteristics of the biocidal compounds (Luttik et al., 1993).

Therefore, most of the chemicals and additives in textile are released to waste water. The waste water is by far the largest waste stream, and it is generated by: washing and rinsing cycles, bath dumps, and equipment clean-up. Operations that represent the greatest concern are finishing and dyeing (Tissier et al., 2001).

The primary route for TCS to enter the environment after its use is through discharge of effluent from wastewater treatment plants and in the effluent due to its incomplete removal in wastewater treatment plants, as well as in the sludge generated in wastewater treatment plants due to its hydrophobic nature (Reiss

et al., 2002; Singer et al., 2002; Ying and Kookana, 2007). The data available in the literature suggests that the concentration of triclosan in effluents can range from 35 ng/L to 2700 ng/L (Reiss et al., 2002; Singer et al., 2002; Ying and Kookana, 2007).

TCS is washed or rinsed off and may enter the environment via local water waste treatment plants (WWTPs); of this, 90% to 98% is typically removed from the water phase as a result of biodegradation and sorption (Orvos et al., 2002; Singer et al., 2002). Nevertheless, U.S. monitoring survey revealed that TCS was commonly detected in surface water at a frequency of 58% and at concentrations ranging from 0.2 to 2.7 µg/L (Reiss et al., 2002). In addition to this, methyl-triclosan (M-TCS), a metabolite of TCS, may be found. M-TCS is more lipophilic and environmentally persistent than the parent compound (Bester, 2003). Concentrations of M-TCS are generally higher in WWTPs effluent than influent, indicating formation of this transformation product in the treatment process.

Considering the low probability of triclosan being released into household wastewater and surface waters from EPA-regulated antimicrobial uses, the Agency concluded that chronic aquatic risks are unlikely originating from consumer uses of triclosan-treated plastic and textile items (EPA, 2008). Therefore, the Agency assumed that the antimicrobial uses of triclosan (e.g., triclosan-treated plastic and textile items in households) are unlikely to contribute significant quantities of triclosan into household wastewater and eventually in surface water.

As stated above, TCS is a broad-spectrum antimicrobial compound used in many different products including toothpaste, shampoos, deodorants, household cleaners, textiles (sportswear, bed clothes, shoes, and carpets) and children's toys (Singer et al., 2002). The concentration of TCS in these products is usually in the range of 0.1% to 0.3% (Amorim et al., 2010).

Triclosan is able to form low chlorinated dioxins on incineration and under the influence of sunlight, under certain circumstances even more highly chlorinated isomers (Adolfsson-Erici et al., 2002).

**Environmental fate**

Triclosan is susceptible to biodegradation, particularly under aerobic conditions. Degradation products include 2,4-dichlorophenol and 2,8-dichlorodibenzo-*p*-dioxin, both of which are further degraded and do not accumulate in fish tissues (Lyndall et al., 2010). These degradation products are less toxic than triclosan (EPA 2009) and are expected to occur at lower concentrations. Quantitative structure activity relationship (QSAR) models suggested an extended environmental half-life of TCS on the order of 540 d upon deposition in aquatic sediment (Lyndall et al., 2010).

It is known that TCS can be degraded in soils under aerobic conditions and that during bacterial degradation TCS is transformed to methyl triclosan (Lozano et al., 2010). Also there are some evidence that TCS can be biodegraded by soil bacteria and fungi. Additional work should be conducted to assess biodegradation rates in the soil environment and determine of the fate of these biodegradation products (Lozano et al., 2010).

TCS has a trichlorinated binuclear aromatic structure which shares similarities with dioxins (Latch et al., 2003), suggesting potentially problematic properties including persistence and bioaccumulation.

Photolytically, triclosan degrades rapidly under continuous irradiation from artificial light at 25°C in a pH 7 aqueous solution, with a calculated aqueous photolytic half-life of 41 minutes.

In soil, triclosan is expected to be immobile based on an estimated organic carbon–water partitioning coefficients (log Koc) of 3.8–4.0 (Lindstrom et al., 2002)

and is not expected to volatilize from soil or water surfaces based on its estimated Henry's Law (1.5 x 10-7 atm m3 mol-1) (EPA, 2008).

Agüera et al. (2003) analysed wastewater samples, coming from an urban wastewater treatment plant (UWWTP), and marine sediment samples collected at the outflow of two UWWTPs to the sea. Results obtained revealed the presence of triclosan in all the samples. These results corroborated that triclosan is emitted via UWWTPs to the marine environment and it is accumulated in the sediments, been susceptible to produce unpredicted effects in the marine ecosystem. The removal rates for TCS in five selected WWTPs were found to range between 72% and 93% (Ying and Kookana, 2007). Biological degradation was believed to be the predominant removal mechanism for TCS in the WWTPs. However, adsorption onto sludge also played a significant role. TCS at concentrations up to 75 ng/L was detected in surface waters (outfall, upstream, and downstream) from five rivers receiving effluent discharge from WWTPs (Ying and Kookana, 2007).

Most peer-reviewed studies on the fate of TCS in sewage treatment plants (STPs) focused exclusively on aqueous phase concentrations. Concentrations found in these studies ranged from 1–16 µg/L in influent and 0.03– 2.7 µg/L in effluent, suggesting removal efficiencies of 58–97% for trickling filter plants and 95–98% for activated sludge plants (Thomas and Foster, 2005; Heidler and Halden, 2007). Despite the high potential of TCS for particle sorption, concentrations of the compound in sludge were rarely determined, presumably due to the analytical challenge of reliably quantifying the chemical in this difficult matrix (Heidler and Halden, 2007).

Heidler and Halden (2007) explored the persistence of TCS in a typical full-scale activated sludge US sewage treatment plant. Conventional sewage treatment was demonstrated to be much less effective in destroying the antimicrobial than the aqueous-phase removal efficiency of the plant would make believe. Furthermore, study findings indicated that the common practice of sludge

recycling in agriculture results in the transfer of substantial quantities of TCS to US soils used, in part, for animal husbandry and crop production.
In aquatic environments, TCS is expected to adsorb to suspended solids and sediments and may bioaccumulate (log Kow 4.8), potentially posing a concern for aquatic organisms (Orvos et al., 2002).

These data indicate triclosan is not likely to contaminate surface or ground waters due to its immobility in soils, and susceptibility to photodegradation, and potentially biodegradation in soil and water. The majority of published studies on the occurrence of triclosan in waste water treatment plants, treatment plant efficiency, and open water measurements of triclosan suggest that aerobic biodegradation is one of the major and most efficient biodegradation pathways (EPA, 2010).

#### 7.4.1.1 Effects assessment

Although TCS has not been reported to be toxic to mammals, it is toxic to aquatic organisms such as Daphnia magna with a 48-h median effective concentration ($EC_{50}$) of 390 µg/L, fish (Pimephales promelas) with a 96-h median lethal concentration ($LC_{50}$) of 260 µg/L (Orvos et al., 2002), rainbow trout ($LC_{50}$= 350 µg/L) (Adolfsson-Erici et al., 2002). It is of major concern that TCS is very toxic to some algae species (e.g. Scenedesmus subspicatus) with a reported no-observed-effect concentration (72-h growth NOEC) of 500 ng/L (Reiss et al., 2002) and $EC_{50}$ =1.5 µg/L. Algae form an important food source for numerous other organisms. There is also a low-to-moderate potential for bioconcentration in aquatic organisms based on a BCF range of 2.7 to 90 (EPA, 2010). Also its methylated form has been shown to bioaccumulate in organisms such as fish and water plants (Orvos et al., 2002).
Amorim et al. (2010) assessed the toxicity of TCS in the terrestrial environment, using a battery of soil species, belonging to different taxonomic levels, including different species of invertebrates and plants. For the invertebrate species the reproduction $EC_{10}$ ranged between 0.6 and 7mg TCS/kg soil dry weight. For

plants' emergence $EC_{10}$ resulted 0.1 (B. rapa) and 142 (T. aestivum) TCS/kg soil dry weight. The calculated PNEC (Predicted No Effect Concentration) ranged between 0.0008 and 0.004 mg TCS/kg and between 0.04 and 0.2 mg TCS/kg soil dry weight (50% certainty) when using the SSD (Species Sensitivity Distribution) approach; applying a safety factor to the lowest $EC_{10}$ resulted in a PNEC of 0.06 mg TCS/kg soil dry weight.

In regard to the terrestrial environment, TCS may enter soil primary through sludge-amendment. Once in the soil, it mostly remains in the upper 10–20 cm incorporation layer but can degrade with half-lives ranging from 2 to 35 days (Reiss et al., 2009). A maximum of 0.833 mg/kg soil was reported (apparently from a site which was only amended years before the sampling year), in other sites the concentrations were 0.160 and 0.960 mg TCS/kg at day 31 and 156, respectively, after biosolid applications (Kinney et al., 2008). Other studies showed values of TCS below 0.02mg TCS/kg dry weight soil (Xua et al., 2008).

TCS is also known to adsorb to soil and sediment but terrestrial toxicity data for TCS are limited, as confirmed by Liu et al. (2009) who provided data on the effect on soil microbial processes. The results showed that triclosan inhibited plant growth in soil, with rice seeds being more sensitive than cucumber seeds with EC50 values of 57 and 108 mg/kg. Soil respiration was significantly inhibited in the treatments with triclosan at concentrations more than 10 mg/kg (dry soil) during the first 4 days of incubation, but recovered later on after longer incubation. Phosphatase activity was also inhibited for all the soils treated with triclosan (from 0.1 to 50 mg/kg dry soil), but a declining inhibition was observed after 2 days of incubation. Biolog analysis found that triclosan treatment increased the utilization of carbon sources and exerted no adverse effects on the functional diversity of soil microbial community (Liu et al., 2009).

In vitro experiments showed that TCS caused a significant reduction of Chlamydomonas and chroococcalian cyanobacteria at a concentration of 150 ng/L (Wilson et al., 2003).

#### 7.4.1.2 Risk characterization

A qualitative environmental risk assessment was developed using monitoring levels of triclosan found in waterways and toxicity values to develop risk quotients (RQs) and compare them to levels of concern (LOCs) for triclosan. LOCs were not exceeded for fish or aquatic plants. There were no acceptable acute toxicity studies for freshwater invertebrates or estuarine and marine organisms nor were there any acceptable chronic toxicity studies available for aquatic organisms (EPA, 2008). Ying and Kookana, (2007) found he highest TCS concentration in the streams was 75 ng/L from a discharge point.

The lowest 72-h growth NOEC value for S. subspicatus was 500 ng/L (Orvos et al., 2002; Reiss et al., 2002). Based on the aquatic data available (Orvos et al., 2002; Reiss et al., 2002) and EU's Technical Guidance Document on Risk Assessment (EC, 2003), an assessment factor of 10 is chosen, a predicted no effect concentration (PNEC) of 50 ng/L is obtained for TCS in freshwater aquatic environment, based on the worst-case scenario, 75 ng/L was used as the predicted environmental concentration (PEC). The risk quotient (RQ) for surface water can be calculated based on the above PEC and PNEC values, and the RQ value is 1.5. As the RQ value is more than 1, this indicates that discharge of wastewater to streams with low flow may lead to risk of effects on aquatic organisms such as algae. But if the average TCS concentration of 33 ng/L in the streams is chosen as PEC, the RQ value becomes less than 1. That means the risk from TCS is acceptable.

Application of biosolids on land could lead to TCS contamination of soil. The TCS concentrations in Australian biosolids were found to range from 0.09 mg/kg to 16.79 mg/kg (Ying and Kookana, 2007). The highest concentration of 16.69 mg/kg in biosolid can be used to estimate the PEC value in a worst-case scenario. Ying and Kookana, (2007) assumed that the biosolid application rate was 10 t/ha, the plough depth was 10 cm and the soil bulk density was 1.3 g/cm3; which results in a dilution factor of 130. Therefore, the PEC value was esti-

mated to be 0.13 mg/kg in soil. A seedling growth test with six plants species (corn, ryegrass, wheat, cucumber, soybean and tomato) showed that cucumber was the most sensitive species to TCS with a NOEC of 96 µg/kg (Ying and Kookana, 2007). Little terrestrial toxicity data is available in the literature. Thus, the NOEC value for cucumber and an assessment factor of 1000 were used to estimate PNEC for the terrestrial risk assessment (EC, 2003), and the PNEC value is 0.096 µg/kg. Based on the above PEC and PNEC values, the risk quotient is calculated to be 1360, which is considerably more than 1. Therefore, the TCS concentration in biosolids could cause effects in soil if biosolids were applied on land. However, more information on its toxicity to terrestrial organisms and its fate in the soil environment is needed in order to conduct a more realistic environmental risk assessment.

### 7.4.2 Human health

#### 7.4.2.1 Exposure assessment

Usually only the colorants, the finishing agents including coating, carpet backing, binders and other additives remain on the textile substrates, whereas most of the other applied substances, which are necessary to enable/enhance the pre-treatment, dyeing, printing, and finishing processes are emitted to a great part to the waste water. Thus emissions to water are predominant (OECD, 2004). Substances remain intended (dyestuffs, optical brighteners, functional finishing agents) and non-intended on the textiles are delivered to the consumer.

### 7.4.3 Effects assessment

The toxicology database for triclosan is complete. The following information was taken from EPA (2008), which carried out a complete risk assessment for triclosan.

Acute toxicity studies in experimental animals show that by the oral and dermal routes, triclosan is of low acute toxicity (Acute Oral- Rat LD50: >5000 mg/kg; Acute Dermal- Rabbit LD50: >9300 mg/kg). By the inhalation route of exposure, triclosan is of higher acute toxicity by inhalation exposure than by oral or dermal exposures (Acute Inhalation- Rat LC50: >0.15 mg/L). Triclosan produces moderate irritation to the eyes and skin (Primary Eye Irritation- Rabbit: moderately irritating). Triclosan was not a dermal sensitizer in guinea pigs (EPA, 2008).

Liver toxicity was noted after repeated oral dosing of triclosan to rats, mice, and dogs (in the 90-day rat study, at a dose of 50 mg/kg/day; in the 28-day mouse study, at doses of 135 and 158 mg/kg/day for male and female respectively; in a 90-day oral toxicity study in dogs at a dose of 25 mg/kg/day).

Dermal irritation was noted after repeated dermal exposure in a 90-day dermal toxicity study in rats (irritation at 10 mg/kg/day and a NOAEL for systemic effects at 40 mg/kg/day) and two 14-day dermal toxicity studies in mice (NOAEL of 0.6 mg/animal/day).

Repeated exposure by the inhalation route resulted in inflammation of the respiratory tract as well as changes in several serum enzymes. A LOAEL of 50 mg/m3 or 3.21 mg/kg/day was observed in male rats and no NOAEL was established in males.

Developmental toxicity testing of triclosan in rats and rabbits showed no evidence of pre- or postnatal developmental toxicity at any dose level in either study up to and including 300 mg/kg/day. Developmental LOAELs were therefore not identified. In 2-generation reproductive toxicity testing of triclosan in rats showed effects in offspring (decreased viability and weaning index) only at doses producing toxicity in parental animals (decreased body weights).

Chronic toxicity testing of triclosan in baboons showed signs of clinical toxicity at a dose of 100 mg/kg/day with a NOAEL of 30 mg/kg/day. Chronic toxicity

testing of triclosan in hamsters showed increased mortality, decreased weight gain at a dose of 250 mg/kg/day with a NOAEL of 75 mg/kg/day. In carcinogenicity testing in rats there was no evidence of a carcinogenic effect. In several mutagenicity tests, triclosan was negative for mutagenicity.

In a metabolism study in hamsters, urine was the major route of elimination for triclosan radioactivity. In a metabolism study in mice, triclosan was eliminated primarily through the feces. In metabolism studies conducted in rats, dogs, and rabbits, results indicated that at least 70% of an oral dose of triclosan is absorbed from the gastrointestinal tract and that biliary secretion and subsequent fecal elimination is a major excretory route in the rat and dog. Urinary excretion appeared to be a major route of elimination in the rabbit.

In 2007, the Health Effects Division Carcinogenicity Assessment Review Committee met and classified triclosan as “not likely to be carcinogenic to humans.

In a study conducted by Adolfsson-Erici et al.(2002), high levels of TCS was found in three out of five randomly selected human milk samples. It was also found in the bile of fish exposed to municipal wastewater and in wild living fish from the receiving waters of the three wastewater treatment plants. These findings indicated that substantial amounts of triclosan are released into the environment, which can create unwanted effects. Due to its specific action, it can foster resistant bacteria and it may also be connected with the increase of allergies. Dioxins may be formed when manufacturing triclosan and when incinerating products containing triclosan. Evidence from in vitro studies suggests that TCS may act as an endocrine disruptor (Jacobs et al., 2005; Schuur et al., 1998). In humans, permanent exposure and bioaccumulation was demonstrated, respectively, via detection of TCS in urine (6702 µg/L) and breast milk (6300 µg/kg lipid weight) (Adolfsson- Erici et al., 2002). Additional studies conducted in vitro showed that exposure to TCS inhibits phase II enzyme metabolism in human liver (Wang et al., 2004).

#### 7.4.3.1 Risk characterization

EPA carried out human health risk assessment for triclosan (EPA, 2008). All exposure durations were assessed using the selected oral NOAEL of 30 mg/kg/day with a target MOE (margine of exposure) of 100. The oral endpoint was selected to represent the various oral exposure scenarios that are expected from antimicrobial exposure to triclosan (EPA, 2008). The aggregate risks to triclosan from all uses do not trigger a risk of concern. The mean MOEs range from 4,700 to 19,000. The MOEs at the 99th percentile range from 260 to 1,500.

Triclosan short-term dermal irritation exposures and risks were not estimated for occupational handler exposures. Instead, dermal irritation exposures and risks will be mitigated using default personal protective equipment requirements based on the toxicity
of the end-use product. For intermediate-term dermal risks, the MOEs were above the target MOE of 100, and therefore, not of concern except for commercial painters and material preservative use.

For the occupational handler inhalation exposure and risk assessment, the MOEs were
below the target of 1000. Based on the low vapor pressure of triclosan inhalation post-application exposure is expected to be minimal (EPA, 2008).

EPA evaluated the submitted toxicology, product and residue chemistry, and occupational/residential exposure studies as well as available open literature and determined that the data were adequate to support this reregistration eligibility decision.
Dietary exposure and risk were assessed for the indirect food uses of triclosan. Products containing triclosan are largely used indoors as a materials preservative. However, there is potential for effluents from products containing this chemical to contact fresh water environments. Triclosan was detected in both

raw and finished drinking water in Southern California at levels of 56 and 49 ng/L, respectively. Using the assumption of 2L consumption per day for adults, the intake of triclosan is estimated at 98 ng/person/day or 1.4 ng/kg/day for a 70 kg adult. Comparing this intake value to the selected reference dose for triclosan (0.3 mg/kg/day or 300,000 ng/kg/day), the intake of triclosan in drinking water using the measured value does not present a risk of concern. Triclosan degrades with an average half-life value of 5.2 ± 1.7 days. Therefore, the potential for effluents from products to impact drinking water sources is negligible. Therefore a quantitative drinking water assessment was not conducted.

Non-cancer dietary risk is expressed as a percentage of a level of concern. This dietary level of concern is termed the population adjusted dose (PAD), which reflects the reference dose (RfD), either acute or chronic, adjusted for (divided by) any database uncertainty (special sensitivity) factor. In the case of triclosan, the special sensitivity factor is 1 (estimated risks that are less than 100% of the PAD are below EPA's level of concern). The acute PAD (aPAD) is the highest predicted dose to which a person could be exposed on a single day with no expected adverse health effect. The chronic PAD (cPAD) is the highest predicted dose to which a person could be exposed over the course of a lifetime with no expected adverse health effect.

Using conservative assumptions, the Agency estimated dietary exposure to triclosan when used in adhesives, pulp and paper, cutting boards and conveyer belts. Because the aPAD and cPAD are well below 100%, dietary exposure does not exceed the Agency's level of concern.

# 8 Flame retardants (HBCD)

## 8.1 *Introduction*

After a preliminary study carried out within the framework of the WP5 of the RISKCYCLE project, hexabromocyclododecane (HBCDD) was highlighted as one important additive used in the textile sector. For this reason, a study is presented in this document on its environmental and human health risk.

### 8.1.1 Technical HBCDD

Three diastereomers (α-, β- and γ- HBCDD), which exist as pairs of enantiomers (Figure 14), are mainly found in technical HBCDD. The final distribution of the diastereomers in the technical product varies with a range of about 70-95% γ--HBCDD and 5-30% α - and β-HBCDD.

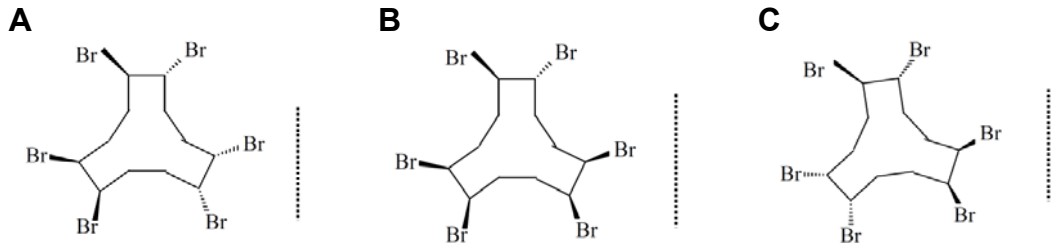


**Figure14. Main diastereomers (pairs of enantiomers) in technical product of HBCDD: A) α -HBCDD; B) β -HBCDD; C) γ-HBCDD. The lines indicate a mirror plane (ECB (European Chemicals Bureau), 2008).**

### 8.1.2 Physical and chemical properties of HBCDD

A summary of the physico-chemical properties of technical HBCDD are shown in Table 23.

**Table 23. Physical and chemical properties of technical HBCDD (ECB, 2008).**

| Property | Value |
|---|---|
| CAS No | 25637-99-4 (mixture of mainly 3 diastereomers) |
| Chemical formula | $C_{12}H_{18}Br_6$ |
| Molecular weight | 641.7 |
| Melting point, °C | Ranges from 172-184 °C to 201-205 °C (Smith et al., 2005)<br>Average value used in the risk assessment of the ECB (ECB, 2008) = 190 °C |
| Boiling point, °C | Decomposes at > 190 °C (Peled et al., 1995) |
| Property | Value |
| Vapour pressure, Pa | $6.3 \cdot 10^{-5}$ (21 °C) (Stenzel and Nixon, 1997) |
| Water solubility at 20 °C, µg/L | 66 (sum of α-, β- and γ- HBCDD) (MacGregor and Nixon, 2004) |
| Density, g/cm$^3$ | 2.38 (Albemarle Corporation, 1994)<br>2.24 (Great Lakes Chemical Corporation, 1994) |
| Henry's law constant, Pa m$^3$ mol$^{-1}$ at 20 °C | 0.75 (calculated from the vapour pressure and the water solubility (66 µg/L)) |
| Log $K_{ow}$ at 25 °C | 5.62 (MacGregor and Nixon, 1997) |

### 8.1.3 Uses of HBCDD

HBCDD is used industrially with the aim to increase the flame resistance of different end-products. Its main uses are in the polymer and textile industries. HBCDD can be used on its own or in combination with other flame retardants, e.g. antimony trioxide and decabromodiphenyl ether (decaBDE).

HBCDD is used in four principal materials. Its main uses, according to the product type, are shown in Table 24. According to industry information, 90% of HBCDD is mainly employed in the production of polystyrene (PS) and the predominant final products are rigid insulation panels/boards for construction (Table 24).

**Table24. Use pattern of HBCDD (ECB, 2008).**

| Percentage of use | Material | End-products |
|---|---|---|
| 88% | Expandable Polystyrene (EPS) | • Construction boards<br>• Insulation boards (e.g., of transport vehicles, in building constructions, against frost heaves of road and railway embankments)<br>• Packaging material (minor use and not in food packaging) |
| | Extruded Polystyrene (XPS) | • Construction boards<br>• Insulation boards (e.g., of transport vehicles, in building constructions, against frost heaves of road and railway embankments) |
| 2% | High Impact Polystyrene (HIPS) | • Electric housing for video cassette recorders<br>• Electrical and electronic equipment (e.g. distribution boxes for electrical lines)<br>• Video cassette housing |
| 10% | Polymer dispersion on cotton or cotton/synthetic blends | • Upholstery fabric<br>• Bed mattress ticking<br>• Flat and pile upholstered furniture (residential and commercial furniture)<br>• Upholstery seating in transportation<br>• Draperies and wall coverings<br>• Automobile interior textiles |

## 8.2 *Risk characterization related to HBCDD*

Risk characterization is the estimation of the incidence and severity of the adverse effects likely to occur in a human population or an environmental compartment due to actual or predicted exposure to a substance. It generally involves the integration of the following steps: exposure assessment, effects assessment and risk estimation (van Leeuwen and Vermeire, 2007). Each one of these steps is treated in the following subsections. In the first one, the environmental risk characterization is presented. The human health risk is characterized in the following one.

### 8.2.1 Environment

#### 8.2.1.1 Exposure assessment

In general, exposure assessment involves estimating emissions, pathways and rates of movement of a substance and its transformation or degradation in order to obtain concentrations or doses to which environmental compartments or human populations are or may be exposed (van Leeuwen and Vermeire, 2007).
The environment may be exposed to chemical substances during all stages of their life-cycle, from production to disposal or recovery. For each environmental compartment potentially exposed (air, soil, water, sediment) the exposure concentrations must be derived. The assessment procedure should in principle consider the following stages of the life-cycle of a substance:

- Production
- Transport and storage
- Formulation (blending and mixing of substances in preparations)
- Industrial/Professional use (large scale use including processing (industry) and/or small scale use (trade))
- Private or consumer use
- Service life of articles
- Waste disposal and recycling

HBCDD is used industrially in several life cycle steps (production, transport, formulation, industrial use). The end-products containing HBCDD are used both professionally and by consumers. They have a relatively long service life and are disposed of by different means (incinerated, recycled, put on landfill or left in the environment). In all these life cycle stages, releases to the environment can be expected.

The risk assessment developed by the European Chemicals Bureau (ECB, 2008) represents the most up-to-date and comprehensive work on the risk characterization of this chemical. In this work different scenarios associated to several life cycle steps of this substance were considered. In Table25 the stud-

ied scenarios are shown (considering that production and micronising represent a unique scenario, nine of them are presented). Scenarios associated with the distribution and transport of HBCDD were not covered in this risk assessment. According to the reporters, data on this issue, and on the associated releases thereby, are lacking. Other scenarios not covered in this work were related to the diffuse release from waste and waste management, and recovery and recycling. This was due to the fact that concentrations in the environment for this type of releases are not specifically covered in the Technical Guidance Document (TGD) on Risk Assessment of the European Commission (EC, 2003). However, existing measured levels in leachate water from landfill were included in the risk assessment.

Data on the emission factors of HBCDD to water and air, and on the amount of HBCDD used annually in different European sites were provided by the industry in ECB (2008) (see Table 25). These data allowed the reporters to estimate concentrations of HBCDD on the different environmental compartments (freshwater, marine water, sediment, soil, etc.) (Predicted Environmental Concentration – PEC) according to the data and equations included in the Technical Guidance Document (TGD) and by using the EUSES software (EUSES, v.2.0). An example on how to compute a PEC value for the water compartment is included in the Appendix B (Example 1).

**Table 25. Risk assessment for HBCDD of the ECB (2008): scenarios considered and overview of site-specific information available.**

| Life-cycle stage | Scenarios | Number of sites in EU | Number of sites with data provided | | |
|---|---|---|---|---|---|
| | | | *Type of data provided* | | |
| | | | *HBCDD volume per site* | *Emission to water* | *Emission to air* |
| Production | Production | 1 | 2 (1) | 2 (1) | 2 (1) |
| | Micronising | Few | 1 | 1 | 1 |
| Formulation | Formulation of PS compound for the manufacture of EPS and/or HIPS | > 18 (EPS) 4 (HIPS) | 13 | 5 | 2 |

| | | | | | |
|---|---|---|---|---|---|
| | Formulation of XPS compound for the manufacture of flame retarded XPS | > 14 | 2 | 2 | 2 |
| | Formulation of polymer dispersions for textile backcoating | 16 | 6 | 4 | 2 |
| Industrial use | Industrial use of EPS compound at the manufacture of flame retarded EPS | Hundreds | -- | -- | -- |
| | Industrial use of HIPS compound at the manufacture of flame retarded HIPS | NA | -- | -- | -- |
| | Industrial use of XPS compound at the manufacture of flame retarded XPS | 17 (A) | 5 | 5 | 5 |

| **Life-cycle stage** | **Scenarios** | **Number of sites in EU** | **Number of sites with data provided** | | |
|---|---|---|---|---|---|
| | | | ***Type of data provided*** | | |
| | | | ***HBCDD volume per site*** | ***Emission to water*** | ***Emission to air*** |
| Industrial use | Industrial use of HBCDD-powder at the manufacture of flame retarded XPS | 18 | 18 | 18 | 1 |
| | Industrial use of polymer dispersion at the backcoating of textile | 24 | 5 | 4 | 4 |

A: Assumption

NA: Not Available

(1) One site closed in December 2003

## Environmental fate

Experimental studies have been developed to evaluate the biodegradation and the environmental distribution of HBCDD. In accordance with the information presented in ECB (2008), general conclusions drawn from these studies are described in the followings subsections. For an extended description of the experimental methodologies, check this last mentioned reference.

### A. Biodegradation

HBCDD is not readily biodegradable. The following results were observed in the two main simulation biodegradation studies:

- Study 1 (Davis et al., 2003): The HBCDD concentrations used in this study (34-89 μg/kg dwt) are representative of the levels normally found in the sediment. A dissipation half-life of around 20-60 days at 12°C was obtained for γ-diastereomer in aerobic sediment (α- and β-diastereomers were not studied). It is not certain that the disappearance in this study only reflects biodegradation because, as reported by the authors, problems with the extraction method were detected. Therefore, half-lives obtained may not be completely certain.
- Study 2 (Davis et al., 2004): High HBCDD concentrations in sediments were used in this study (up to 100-fold higher than in Study 1). In aerobic sediment, approximately half of the added HBCDD was transformed into three dehalogenated metabolites (tetrabromocyclododecene, dibromocyclododecadiene and 1,5,9-cyclododecatriene (CDT)) within 4 months at 20°C. The half-lives of the individual diastereomers were approximately 210, 130 and 200 days for α-, β- and γ- HBCDD, respectively, when temperature was corrected to 12°C. Although reliable data were obtained in this study, concentrations were not as realistic as those from Study 1.

In simulation Study 2 it was shown that HBCDD was degraded via stepwise dehalogenation to CDT (the raw material for production of HBCDD). Therefore, the degradability of this metabolite was also studied (Davis, 2006). It was observed that up to 70% carbon dioxide was formed during 70 days of incubation. This was interpreted as evidence that CDT is not readily biodegradable, but does not fulfill the persistence criterion of the TGD.

## B. Environmental distribution

Experimental data on the environmental distribution of HBCDD have been summarized as:

- **ADSORPTION:**
  - HBCDD is predicted to adsorb to soil based on its water solubility, log $K_{ow}$ and vapour pressure.
  - A log $K_{oc}$ value can be calculated from:
    $\log K_{oc} = 0.81 \cdot \log K_{ow} + 0.10 = 4.66$.
  - This indicates a very high potential to adsorb to soils and sediment, and a low potential to leach through soil.

- **VOLATILISATION:**
  - No specific studies on the volatilization of HBCDD were identified.
  - HBCDD has a low potential to evaporate from aquatic surfaces.
  - Evaporation of HBCDD seems to be a less important route of dispersion.
  - HBCDD has a very low potential to reach remote areas (Wania, 2003).

- **ELIMINATION IN SEWAGE TREATMENT PLANTS (STP):**
  - According to the results of the Simple Treat Model, which is a part of the EUSES model, the overall removal of HBCDD in a STP is approximately 80% (major part is expected to be adsorbed to the sludge).

- **BIOACCUMULATION:**
  - The study of Veith et al. (1979) gave a Bioconcentration Factor (BCF) for the fathead minnow fish of 18100, but it was performed without agreed standardized test procedures.
  - In the study on rainbow trout of Drottar and Krueger (2000), BCF values ranged between 8974 and 21940.

- BCF values were considered to support each other and the value of 18100 was considered for fishes by ECB (2008).

- **BIOMAGNIFICATION:**
  - Measurements of HBCDD in the environment indicate that HBCDD biomagnifies.
  - It is not possible to determine definite biomagnification factors.

#### 8.2.1.2 Effects assessment

Data on the environmental effects of HBCDD are summarized in Table 31 (Appendix A). These data are from studies considered valid by the ECB. For the aquatic compartment, reliable data were available on the toxicity to organisms at a three trophic levels; the lowest NOEC was for *Daphnia magna* (3.1 μg/L). Since chemicals may cause adverse effects on microbial activity in STPs, generally this is also considered as an environmental compartment. An $EC_{30}$ value of 15 mg/L was obtained in a respiration inhibition test.
For sediments, there were chronic results from three species with different feeding regimes. The lowest NOEC was for worms (*Lumbriculus variegates*) (8.61 mg/kg dw). NOEC values for the terrestrial compartment were derived for long-term toxicity tests for more than three species, the lowest value being for earthworms (59 mg/kg).

#### 8.2.1.3 Risk characterization

Environmental risk is often estimated as a risk quotient, i.e. PEC/PNEC, where PEC stands for 'Predicted Environmental Concentration' and PNEC for 'Predicted No Effect Concentration'. This approach was applied by the ECB on the risk assessment of HBCDD (ECB, 2008).
According to the reliable data available on the acute and chronic ecotoxicity of HBCDD shown in Table 31 (Appendix A), ECB (2008) calculated Predicted No Effects Concentrations (PNEC) to be used in the risk characterization of HBCDD. Different assessment factors were considered for each sub-

compartment. In Table 26 the criteria used to derive the PNEC values from ecotoxicity data are shown, together with the assessment factors employed.

The general results obtained by the ECB (2008) on the environmental risk characterization of HBCDD are summarized in the following table (Table 27). According to this table, textile sites are posing risk to all three compartments, especially to the aquatic. More specifically, for the industrial use of textile backcoating agents, the freshwater sediment sub-compartment is that mainly affected (PEC/PNEC = 270 for a generic site).

In the Appendix B, the derivation of the PEC/PNEC ratio is shown for Example 1, also the associated conclusion drawn from this calculation is explained.

**Table 26. PNECs used in the risk characterization of the ECB (2008) for HBCDD.**

| Compartment | Sub-compartment (symbol) | PNEC value | Derivation [1] |
|---|---|---|---|
| Aquatic | Freshwater ($PNEC_{water}$) | 0.31 μg/L | An assessment factor of **10** was applied on the lowest NOEC, because reliable NOEC values were available for the three trophic levels. |
| | Freshwater - Intermittent release ($PNEC_{intermittent\ water}$) | 0.52 μg/L | An assessment factor of **100** was applied on the lowest $EC_{50}$ of three short-term tests from three trophic levels. |
| Aquatic | Micro-organisms (STP) ($PNEC_{STP}$) | 0.15 mg/L | An $EC_{30}$ obtained at 15 mg/L was taken as an estimate for the $EC_{50}$ for the PNEC derivation. An assessment factor of **100** was used according to EC (2003). |
| | Sediment ($PNEC_{sediment}$) | 0.86 mg/kg dwt | An assessment factor of **10** was applied on the lowest NOEC value and then normalized to 5% organic carbon content in the sediment. |
| Terrestrial | Soil ($PNEC_{soil}$) | 5.9 mg/kg dry soil | A normalized NOEC value for the reproduction of earthworms is used, after applying an assessment factor of **10** (EC, 2003). |
| Atmosphere | Air ($PNEC_{air}$) | -- | There are no effect data available for the atmospheric environment. |
| Non | Oral ($PNEC_{oral}$) | 5 mg/kg food | For assessment of secondary poisoning, the concentration in food |

| | | | |
|---|---|---|---|
| compartment specific | | | causing no effects was derived from a NOAEC value for the reproductive toxicity in rats, applying an assessment factor of **30**. |
| Compartment | Sub-compartment (symbol) | PNEC value | Derivation (1) |
| Marine | Marine water ($PNEC_{water,marine}$) | 0.03 μg/L | An assessment factor of **100** was applied on the lowest NOEC from freshwater database. |
| | Marine water - Intermittent release ($PNEC_{intermittent\ water,marine}$) | 0.05 μg/L | An assessment factor of **1000** was applied on the lowest $EC_{50}$ from freshwater database. |
| | Marine sediment ($PNEC_{sediment,marine}$) | 0.17 mg/kg dwt | An assessment factor of **50** was applied on the lowest long-term NOEC of three long-term sediment tests with species representing different living and feeding conditions. |

(1) Assessment factors in bold. Ecotoxicity data used for the derivation of the PNEC refer to those shown in Table31 (Appendix A).

$EC_{\#}$: Effect Concentration measured as #% effect; NOAEC: No Observed Adverse Effect Concentration; NOEC: No Observed Effect Concentration

**Table 27. Environmental risk characterization results (ECB, 2008).**

| **Compartment** | **Sub-compartment** | **Risk quotient** | **Sites with the corresponding type of quotient (1)** |
|---|---|---|---|
| Aquatic | In either surface water or sediment, or in both compartments | > 1 | Sites involved in EPS and XPS formulation, **formulation of polymer dispersions for textiles**, industrial use of XPS, and **sites involved in textile backcoating** |
| | In both surface water and sediment | < 1 | Sites with production, micronising and industrial use of EPS, HIPS |
| | Micro-organisms (sewage treatment plants) | > 1 | Some sites with industrial use of XPS having intermittent releases<br>**1 textile backcoating site** |
| Compartment | Sub-compartment | Risk quotient | Sites with the corresponding type of quotient (1) |
| Terrestrial | -- | > 1 | **For generic local scenario for the industrial use** of XPS and **textile backcoating**, and for a few individual sites in these use areas |
| | -- | < 1 | For most use areas |
| Marine | In either surface water or sediment, or in both compartments | > 1 | Sites involved in EPS and XPS formulation, **formulation of polymer dispersions for textiles**, industrial use of XPS, and **sites involved in textile backcoating** |

| | | | |
|---|---|---|---|
| | In both surface water and sediment | < 1 | Sites with production, micronising and industrial use of EPS, HIPS |

(1) Textile sites are in bold.

To see if HBCDD is persistent (P), bioaccumulative (B) and toxic (T), the several criteria established by the EC (EC, 2003) can be considered. The available experimental data associated to these criteria are shown in Table 28. Based on these data, it can be stated that, although the P criterion is not unequivocally fulfilled, HBCDD very much exceeds the bioaccumulation criteria and it fulfills the toxicity criteria. Moreover, it is present in wildlife distant from areas of its use. Thus, it can be concluded that this substance **overall fulfills the PBT-criteria of the TGD**.

**Table 28. PBT- and vPvB-criteria for HBCDD (ECB, 2008).**

| Criterion | PBT-criteria | vPvB-criteria | Results for HBCDD |
|---|---|---|---|
| P | Half-life > 120 d in freshwater sediment | Half-life > 180 d in marine or freshwater sediment | Not readily biodegradable (half-lives > 120 d only at high concentrations; see the specific comments reported previously on Study 2 from Davis et al. (2004)). |
| B | BCF > 2000 | BCF > 5000 | BCF 18100 |
| T | Chronic NOEC < 0.01 mg/L or CMR or endocrine disrupting effects | Not applicable | Chronic NOEC *Daphnia survival*, reproduction, growth 3.1 μg/L<br>Chronic LOEC *Daphnia* reduced length 5.6 μg/L |

## 8.2.2 Human health

### 8.2.2.1 Exposure assessment

Humans may be exposed to HBCDD from different sources and routes (see Table 29), and for different periods during lifetime, including single short-term exposure and persistent exposure for a lifetime.

**Table 29. Sources and routes of exposure to HBCDD depending on the type of population.**

| Population | Sources of exposure | Route |
|---|---|---|
| Workers | • Production of HBCDD<br>• Formulation and industrial use of HBCDD as an additive<br>• Industrial use of articles containing HBCDD | • Inhalation of vapour or airborne dust<br>• Dermal contact<br>• Ingestion<br>• Pregnancy<br>• Breast milk feeding |
| Consumers | • Use of consumer products<br>• Indirectly via the environment (via food, soil, water and air) | |

In the following subsections, exposure scenarios considered by the ECB in the risk assessment of HBCDD (ECB, 2008) are summarized.

### Occupational exposure

There are three sectors were occupational exposure to HBCDD may occur: manufacture of HBCDD, industrial use of HBCDD, and industrial use of semi-finished or end-products containing HBCDD. ECB (2008) considered the following exposure scenarios for occupational risk characterization:

- Filling of bags at the manufacture of HBCDD
- Charging of HBCDD to processes producing end-products or semi-products containing HBCDD
- Sewing

For these scenarios, the reporters of the ECB risk assessment calculated reasonable worst-case exposures by using measured data of HBCDD, as well as physico-chemical data of HBCDD (physical state, powder dimension, vapour pressure). In addition, other data sources were used: data regarding methods and use pattern of the product temperature at which production processes take place and the amount of HBCDD used in the different products. Table 32 in the Appendix A shows the exposure values derived by the ECB for several scenarios and two different routes of exposure: inhalation and dermal.

**Consumers exposure**

ECB (2008) considered several possible consumer exposure scenarios to HBCDD (their main characteristics are shown in the Appendix A (Table 33). Calculated exposure levels were considered insignificant for most of these scenarios (except for the oral exposure by mouthing of textile by children) and therefore were not brought forward to the risk characterization.

**Indirect exposure via the environment**

Since HBCDD is a rather persistent and bioaccumulating substance, it could be expected that the exposure to man via food is an important route of exposure. There are limited data on indirect exposure to HBCDD, with most monitoring/screening being performed in Scandinavia, and recently, in the UK and the Netherlands. Low levels of HBCDD have been found in different fish species (for more information, see Table 4.16 in ECB (2008)) and in food items, such as salmon, egg, milk, vegetable oils and fats, and fat from domestic animals (chicken, beef and lamb) (for more information, see Table 4.17 in ECB (2008)). The average concentration in EU fish could indicate an exposure, for frequent freshwater fish consumers, of 33 ng/kg bwt/day (ECB, 2008). A limited Swedish food basket study indicated a maximum intake of 22 ng HBCDD/kg bwt/day (Sternbeck et al., 2001), and the Dutch study indicated, for a typical diet, an average exposure level of 3 ng/kg bwt/day (De Winter-Sorkina et al., 2003). Based on these data, a typical exposure level of 3, a maximum level of 22, and a reasonable worst case level of 20 ng HBCDD/kg bwt/day were considered in the risk characterization by the ECB (2008).

HBCDD in human breast milk was identified in four Scandinavian studies (for more information, see Table 4.18 in ECB (2008)), the highest concentration measured being of 3.2 ng/g fat. This value was used for calculation of reasonable worst case levels of 15 ng HBCDD/kg bwt/day and 5.6 ng HBCDD/kg bwt/day for infants 0-3 months and 3-12 months old, respectively.

#### 8.2.2.2 Effects assessment

Health effects data of HBCDD have been summarised as the following ones, according to data presented in ECB (2008):

- **TOXICOKINETICS, METABOLISM AND DISTRIBUTION:**
  - HBCDD can be absorbed from the gastro-intestinal tract.
  - The highest concentrations are subsequently reached in adipose tissue and muscles, followed by liver and with much lower activities present in lung, kidney, blood, brain, and gonads.
  - Of the three diastereomers constituting HBCDD, the α-form is much more accumulating than the others (the relative bioaccumulation factor is 99:11:1 for α-, β- and γ- HBCDD, respectively).
  - γ -HBCDD can be metabolised.
  - For an initial period of 3 days post dosing, elimination of HBCDD and its metabolites mainly occurred via faeces with a minor part excreted in urine.
  - Elimination from body fat appears to be markedly slower than from other tissues, with an elimination half-life of the three diastereomers possibly being in the order of weeks to months.

- **ACUTE TOXICITY:**
  - The substance has a very low acute toxicity by the oral and dermal routes of administration.
  - The minimum oral lethal dose (LD) is higher than 20 g/kg in rats, and exceeds 40 g/kg in mice.
  - By the dermal route, $LD_{50}$ is higher than 20 g/kg in rabbits.
  - The acute toxicity by inhalation has not been adequately investigated, but seems low in some technical preparations.

- **IRRITATION AND SENSITISATION:**
  - HBCDD is mildly irritating for the eye, but does not qualify as an eye irritant according to EU criteria.

- The substance is not irritating to skin in skin irritation studies or to the respiratory system according to clinical symptoms in acute toxicity studies by the inhalation route.
- HBCDD is not regarded as a skin sensitizer.
- No data are available to assess the potential for respiratory sensitisation.

- **REPEATED DOSE TOXICITY:**
  - No repeated dose studies with inhalation or dermal exposure as route of administration are available.
  - Five repeated dose studies with oral administration of HBCDD in rats have been conducted; three studies of 28 days and two of 90 days.
  - Repeated dose toxicity studies have shown the liver to be the target organ.
  - A LOAEL of 100 mg/kg/day has been deduced based on a dose-dependent increase in liver weight, although disturbances on the thyroid hormone system also occurred (90-days study).
  - A NOAEL of 22.9 mg/kg/day for liver weight increase was proposed, based on a benchmark model design (28-days study).

- **MUTAGENICITY AND CARCINOGENICITY:**
  - HBCDD lacks significant genotoxic potential in vitro and in vivo.
  - Based on the only available lifetime bioassay, it is not possible to assess the carcinogenic potential of HBCDD. However, the available data (including mutagenicity) gives no reason for further exploration of this endpoint.

- **REPRODUCTIVE/DEVELOPMENTAL (NEURO)TOXICITY:**
  - A NOAEL of 10 mg/kg/day was deduced in a two-generation reproductive toxicity study in rats. The NOAEL was based on dose-

dependent decrease in fertility-index and a reduced number of primordial follicles.

- Two ordinary developmental toxicity studies have failed to demonstrate any fetotoxicity, teratogenic potential or adverse effects from HBCDD on development of rats. However, increased pup mortality during lactation was observed in a 2-generation study.
- A recent study has indicated that neonatal HBCDD exposure may cause developmental neurotoxic effects as illustrated by statistically significant changes in spontaneous behavior, learning and memory defects. An indicative LOAEL of 0.9 mg/kg/day can be deduced from this study, but the results need to be confirmed by other laboratories.

#### 8.2.2.3 Risk characterization

Human health risk is usually characterized by comparing a No Effect Level (NEL) to exposure (van Leeuwen and Vermeire, 2007). Margins of safety (MOS) were calculated in the European risk assessment of HBCDD (ECB, 2008). This variable was obtained according to Eq. (1).

$$MOS = \frac{PTDI}{Exposure\ dose} \quad (1)$$

Where:

| | |
|---|---|
| $PTDI$ | Provisional Tolerable Daily Intake (mg/kg/day) (equivalent to NEL) |
| $Exposure\ dose$ | Dose of exposure estimated (mg/kg/day) |

$PTDI$ values considered by the ECB (2008) were those shown in Table 30. They were derived according to the toxicity effects data of HBCDD on health (described in the Effects Assessment section). Then, exposure doses estimated for the diverse scenarios described in Table 32 (Appendix A) were compared with the two values shown in Table 30 to obtain MOS.

**Table 30. *PTDI* of concern in ECB (2008).**

| Endpoints of concern | Value |
|---|---|
| Repeated dose toxicity | 22.9 mg/kg/day |
| Reproductive toxicity | 10 mg/kg/day |

According to the MOS values obtained by the ECB (2008) for the occupational exposure to HBCDD (see Table 34 and Table 35 of the Appendix A), there is a need for limiting the risks and risk reduction measures which are already being applied should be taken into account. This conclusion was reached because of:

- Concern for repeated dose toxicity effects on the liver as a consequence of inhalation and/or dermal exposure during filling HBCDD fine grade powder in production.
- Concern for reproductive toxicity during filling HBCDD fine and standard grade powder in production, and during adding HBCDD fine and standard powder at industrial use of HBCDD as an additive.

In Examples 2 and 3 of the Appendix B the derived values for MOS are indicated for each of the scenarios considered. The corresponding conclusions to be derived are also included.

For consumers and humans exposed via the environment, the conclusion drawn by ECB (2008) on health risk was that there is at present no need for further information and/or testing and for risk reduction measures beyond those which are being applied already (e.g. limitations in the amount of flame retardant present in products).

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# Appendix A

**Table 31. Reliable acute and chronic ecotoxicity studies.**

| Compartment / Species | Method | Results | Reference |
|---|---|---|---|
| AQUATIC COMPARTMENT | | | |
| **Fish** | | | |
| *Onchorhyncus mykiss* | OECD 203 and TSCA 40/797/1400, and ASTM Standard E729-88a | No mortalities or other effects around 2.5 μg/L | Graves and Swigert (1997b) |
| *Onchorhyncus mykiss* | Flow-through; OECD 210 and OPPTS 850.1400 | NOEC: Hatching success ≥ 3.7 μg/L<br>Swim-up ≥ 3.7 μg/L<br>Larvae and fry survival ≥ 3.7 μg/L<br>Growth ≥ 3.7 μg/L | Drottar et al. (2001) |
| **Invertebrates** | | | |
| *Daphnia magna* | OECD 202. Static immobilisation test, and TSCA 40/797/1300, and ASTM Standard E729-88a | 48 h $EC_{50}$ > 3.2 μg/L | Graves and Swigert (1997a) |
| *Daphnia magna* | TSCA, OECD; Flow through 21 day test | NOEC 3.1 μg/L<br>LOEC length 5.6 μg/L | Drottar and Krueger (1998) |
| **Algae** | | | |
| *Selenastrum capricornutum* | OECD 201 and TSCA 40/797/1050 | 96 h $EC_{50}$ > 2.5 μg/L | Roberts and Swigert (1997) |
| *Skeletonema costatum*<br>*Thallassiosira pseudonana*<br>*Chlorella* sp. | Marine algal bioassay method, different marine growth media (not according to guidelines, results only used as supportive) | 72 h $EC_{50}$ = 9 μg/L (lowest value)<br>72 h $EC_{50}$ = 40 μg/L (lowest value)<br>96 h $EC_{50}$ > water solubility | Walsh et al. (1987) |

**Table 31. (continued).**

| Compartment / Species | Method | Results | Reference |
|---|---|---|---|
| *Skeletonema costatum* | OECD 201, ISO 10253:1995 and EU Directive 92/69/EEC – Method C.3. One test concentration at the limit of respective water solubilities of each diastereomer | NOEC < 40.6 μg/L<br>$EC_{50}$ > 40.6 μg/L | Desjardins et al. (2004) |
| *Skeletonema costatum* | OECD 201. $EC_{50}$ obtained from a limit test with one test concentration (54.5 mg/L) at the limit of respective water solubilities of each diastereomer | NOEC > 10 μg/L<br>$EC_{50}$ = 52 μg/L | Desjardins et al. (2005) |
| SEWAGE TREATMENT PLANT, MICRO-ORGANISMS | | | |
| **Activated sludge** | Respiration inhibition. OECD 209 | $EC_{30}$ = 15 mg/L ($EC_{50}$ = 15 mg/L); Limit test with one test concentration, $EC_{50}$ is estimated. | Schaefer and Siddiqui (2003) |
| SEDIMENT COMPARTMENT | | | |
| **Invertebrates** | | | |
| *Hyalella azteca* (Amphipod) | Sediment toxicity test 28-day exposure period under flow-through conditions | LOEC > 1000 mg/kg dw of sediment<br>NOEC = 1000 mg/kg dw of sediment | Thomas et al. (2003) |
| *Lumbriculus variegates* (Worm) | 28-day sediment bioassay | LOEC = 28.7 mg/kg dw<br>NOEC = 3.1 mg/kg dw<br>Normalized:<br>NOEC = 8.61 mg/kg dw | Oetken et al. (2001) |
| Chironomus riparius (Mosquito) | 28-day sediment bioassay. Egg production of F generation | LOEC = 159 mg/kg dw<br>NOEC = 13.6 mg/kg dw<br>Normalized:<br>NOEC = 37.8 mg/kg dw | Oetken et al. (2001) |

**Table 31. (continued).**

| Compartment / Species | Method | Results | Reference |
|---|---|---|---|
| TERRESTRIAL COMPARTMENT | | | |
| **Plants** | | | |
| Plants: corn (*Zea mays*); cucumber (*Cucumbis sativa*); onion (*Allium cepa*); ryegrass (*Lolium perenne*); soybean (*Glycine max*); tomato (*Lycopersicon esculentum*) | Seedling emergence, height 21 days. OECD 308 (proposal for revision), 850.4100 and 850.4225 (public drafts) | NOEC > 5000 mg/kg dry soil | Porch et al. (2002) |
| **Invertebrates** | | | |
| *Eisenia fetida* (Earthworm) | Survival and reproduction, 56 days. OECD proposed and 207 and OPPTS 850.6200 | NOEC = 128 mg/kg dry soil<br>Normalized:<br>NOEC = 59 mg/kg dry soil ($EC_{50}$ = 771 mg/kg dry soil) | Aufderheide et al. (2003) |

$EC_{\#}$: Effect Concentration measured as #% effect; LOEC: Lowest Observed Effect Concentration; NOEC: No Observed Effect Concentration

**Table32. Exposure data compiled for the occupational risk characterisation based on realistic worst-case exposure concentrations (ECB, 2008).**

| Scenario | Product grade | Inhalation | | |
|---|---|---|---|---|
| | | **Exposure ($mg/m^3$)** | **Assumptions** | **Exposure (mg/kg/day)** |
| FILLING. Filling of bags at the production of HBCDD | Fine powder | 10 | Body weight = 70 kg; Inhalation volume = 10 $m^3$/working day | 1.42 |
| | Powder | 1.9 | | 0.27 |
| | Granules | 0.19 | | 0.03 |
| ADDING. Industrial use of HBCDD as an additive | Formulation of textile. Fine powder | 3.1 | | 0.44 |
| | Formulation of PS (EPS, XPS, HIPS), standard grade powder | 2.5 | | 0.36 |
| | Formulation of polystyrene (EPS, XPS, HIPS), granules masterbatch | 0.22 | | 0.031 |
| SEWING (occupational). Industrial end-use | -- | 0.5 | Body weight = 60 kg; Inhalation volume = 10 $m^3$/working day | 0.08 |
| Scenario | Product grade | Dermal | | |
| | | **Exposure ($mg/m^3$)** | **Assumptions** | **Exposure (mg/kg/day)** |
| FILLING. Filling of bags at the production of HBCDD | Fine powder | 4200 | Dermal absorption = 4%; Body weight = 70 kg | 2.4 |
| | Powder | 840 | | 0.49 |
| | Granules | 84 | Dermal absorption = 2%; Body weight = 70 kg | 0.02 |

**Table 32. (continued).**

| Scenario | Product grade | Inhalation | | |
|---|---|---|---|---|
| | | Exposure ($mg/m^3$) | Assumptions | Exposure (mg/kg/day) |
| ADDING. Industrial use of HBCDD as an additive | Formulation of textile. Fine powder | 120 | Dermal absorption = 4%; Body weight = 70 kg | 0.07 |
| | Formulation of PS (EPS, XPS, HIPS), standard grade powder | 84 | | 0.05 |
| | Formulation of polystyrene (EPS, XPS, HIPS), granules masterbatch | 8.4 | Dermal absorption = 2%; Body weight = 70 kg | 0.002 |
| SEWING (occupational). Industrial end-use | -- | 0.5 | Dermal absorption = 4%; Body weight = 60 kg | 0.08 |

**Table 33. Consumers exposure scenarios considered in ECB (2008).**

| Scenario | Subscenario | Parameters assumed/calculated | Exposure to HBCDD |
|---|---|---|---|
| Textile in furniture (and curtains) | Oral exposure to dust | Textile area = 4 $m^2$<br>Life-time = 10 years<br>Total dust in 10 years = 9.2 g<br>Daily dust available = 2.5 mg/day<br>Content of HBCDD in dust = 0.47 %<br>Population of concern: 10-kg child eating all dust generated | 1.2 μg/kg/day |
| | Inhalation exposure | Emissions during a lifetime (10 years) = 84 mg/$m^2$ textile in dust from the use of textiles<br>Characteristics of the room: volume = 60 $m^3$; area covered with textiles = 4 $m^2$; ventilation rate = 0.35/h<br>Derived release: $3.8 \cdot 10^{-3}$ mg/h<br>Population of concern: adult being in the room 24h; inhalation rate = 20 $m^3$/day; body weight = 60 kg; uptake = 100 % | 1.5 μg/kg/day |
| | Oral exposure by mouthing of textile | Textile area = 50 $cm^2$ fabric back-coated<br>Concentration = 2 mg HBCDD / $cm^2$<br>Duration of the event = 0.5 hours/day<br>0.9% release during 0.5 hours<br>Oral absorption = 100%<br>Population of concern: 10-kg child (1 year old child)<br>One mouthing every 3 days<br>Factor of 10 to consider that the back-coated side is not available | 3 μg/kg/day |

**Table 33. (continued).**

| Scenario | Subscenario | Parameters assumed/calculated | Exposure to HBCDD |
|---|---|---|---|
| Indoor air | Exposure from XPS boards | Characteristics of the boards: area = 50 $m^2$; thickness = 7 cm; density = 40 $kg/m^3$; concentration of HBCDD = 3 % w/w<br>Release factors:<br>1. Estimated: 0.05% w/w during lifetime (20 years); release factor = $2.5 \cdot 10^{-5}$ per year<br>2. Measured: $2.4 \cdot 10^{-7}$ per year<br>Derived release:<br>1. 0.29 mg/24h<br>2. 0.0028 mg/24h<br>Characteristics of the room: volume = 60 $m^3$; area of the walls covered with boards = 50 $m^2$; ventilation rate = 0.35/h<br>Population of concern: adult being in the room 24h; inhalation rate = 20 $m^3$/day; body weight = 60 kg; uptake = 100 % | 1. 0.19 μg/kg bwt/day<br>2. 0.002 μg/kg bwt/day |
| Mattress ticking | Lying down in a bed on a mattress with flame-retarded ticking | Textile area = 2 $m^2$<br>Concentration = 25 % w/w<br>Population of concern: adult lying in the bed 8h/day, 365 days/year; route of exposure = dermal; body weight = 60 kg; uptake = 4 %<br>Weight of the backcoating layer = 350 $g/m^2$<br>Release factor: emission: 0.1 % w/w during lifetime (10 years); release factor = $1 \cdot 10^{-4}$ per year<br>Derived release: $1.6 \cdot 10^{-5}$ g/day | 0.01 μg/kg bwt/day |

**Table 34. Compilation of data from the occupational risk characterisation based on realistic worst-case exposure concentrations. Endpoint of concern: repeated dose toxicity (RDT) (ECB, 2008).**

| Scenario | Product grade | Inhalation | | | Dermal | | | Multiple routes of exposure | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | Exposure mg/m$^3$ mg/kg/day | $MOS_{RDT}$ | Concl. RDT | Exposure mg/day mg/kg/day | $MOS_{RDT}$ | Concl. RDT | Exposure mg/kg/day | $MOS_{RDT}$ | Concl. RDT |
| FILLING. Filling of bags at the production of HBCDD | Fine powder | 10<br>1.42 | 16 | (iii) | 4200<br>2.4 | 10 | (iii) | 3.82 | 6 | (iii) |
| | Powder | 1.9<br>0.27 | 85 | (ii) | 840<br>0.49 | 47 | (ii) | 0.76 | 30 | (ii) |
| | Granules | 0.19<br>0.03 | 763 | (ii) | 84<br>0.02 | 1145 | (ii) | 0.05 | 458 | (ii) |
| ADDING. Industrial use of HBCDD as an additive | Formulation of textile. Fine powder | 3.1<br>0.44 | 52 | (ii) | 120<br>0.07 | 327 | (ii) | 0.51 | 45 | (ii) |
| | Formulation of PS (EPS, XPS, HIPS), standard grade powder | 2.5<br>0.36 | 64 | (ii) | 84<br>0.05 | 458 | (ii) | 0.41 | 56 | (ii) |
| | Formulation of polystyrene (EPS, XPS, HIPS), granules masterbatch | 0.22<br>0.031 | 739 | (ii) | 8.4<br>0.002 | 1145 | (ii) | 0.033 | 763 | (ii) |

**Table 34. (continued).**

| Scenario | Product grade | Inhalation | | | Dermal | | | Multiple routes of exposure | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | Exposure mg/m$^3$ mg/kg/day | $MOS_{RDT}$ | Concl. RDT | Exposure mg/day mg/kg/day | $MOS_{RDT}$ | Concl. RDT | Exposure mg/kg/day | $MOS_{RDT}$ | Concl. RDT |
| SEWING (occupational). Industrial end-use | -- | 0.5<br>0.08 | 286 | (ii) | 84<br>0.06 | 382 | (ii) | 0.14 | 164 | (ii) |

(ii) There is at present no need for further information and/or testing and no need for risk reduction measures beyond those, which are being applied already.

(iii) There is a need for limiting the risks; risk reduction measures which are already being applied shall be taken into account.

MOS: Margin Of Safety; Minimal MOS for repeated dose toxicity = 20; Minimal MOS for reproductive toxicity = 50.

**Table 35. Compilation of data from the occupational risk characterisation based on realistic worst-case exposure concentrations. Endpoint of concern: reproductive toxicity (REPRO) (ECB, 2008).**

| Scenario | Product grade | Inhalation | | | Dermal | | | Multiple routes of exposure | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | Exposure mg/m$^3$ mg/kg/day | $MOS_{REPRO}$ | Concl. REPRO | Exposure mg/day mg/kg/day | $MOS_{REPRO}$ | Concl. RDT | Exposure mg/kg/day | $MOS_{REPRO}$ | Concl. REPRO |
| FILLING. Filling of bags at the production of HBCDD | Fine powder | 10<br>1.42 | 7 | (iii) | 4200<br>2.4 | 4 | (iii) | 3.82 | 3 | (iii) |
| | Powder | 1.9<br>0.27 | 37 | (iii) | 840<br>0.49 | 20 | (iii) | 0.76 | 13 | (iii) |
| | Granules | 0.19<br>0.03 | 333 | (ii) | 84<br>0.02 | 5000 | (ii) | 0.05 | 200 | (ii) |
| ADDING. Industrial use of HBCDD as an additive | Formulation of textile. Fine powder | 3.1<br>0.44 | 23 | (iii) | 120<br>0.07 | 143 | (ii) | 0.51 | 20 | (iii) |
| | Formulation of PS (EPS, XPS, HIPS), standard grade powder | 2.5<br>0.36 | 28 | (iii) | 84<br>0.05 | 200 | (ii) | 0.41 | 24 | (iii) |
| | Formulation of polystyrene (EPS, XPS, HIPS), granules masterbatch | 0.22<br>0.031 | 323 | (ii) | 8.4<br>0.002 | 5000 | (ii) | 0.033 | 333 | (ii) |

**Table 35. (continued).**

| Scenario | Product grade | Inhalation | | | Dermal | | | Multiple routes of exposure | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | Exposure mg/m$^3$ mg/kg/day | $MOS_{RDT}$ | Concl. RDT | Exposure mg/day mg/kg/day | $MOS_{RDT}$ | Concl. RDT | Exposure mg/kg/day | $MOS_{RDT}$ | Concl. RDT |
| SEWING (occupational). Industrial end-use | -- | 0.5<br>0.08 | 125 | (ii) | 84<br>0.06 | 167 | (ii) | 0.14 | 71 | (ii) |

(ii) There is at present no need for further information and/or testing and no need for risk reduction measures beyond those, which are being applied already.

(iii) There is a need for limiting the risks; risk reduction measures which are already being applied shall be taken into account.

MOS: Margin Of Safety; Minimal MOS for repeated dose toxicity = 20; Minimal MOS for reproductive toxicity = 50.

# Appendix B

In this Appendix there are three examples to show how the risk was characterized for different scenarios. The first example refers to the environmental risk characterization and the last two refer to the human health risk. They were extracted from the ECB risk assessment for HBCDD (ECB, 2008).

**Example 1**

*Risk characterization of the emission of HBCDD to freshwater from a site with formulation of polymer dispersions for textiles (TexForm1 site, according to ECB (2008)).*

The concentration in surface water ($PEClocal_{water}$) is calculated by considering a complete mixing of the effluent outfall. Because of the short time between effluent discharge and exposure location, dilution is considered the dominant "removal" process and a standard dilution factor is used ($DILUTION$). The resulting dissolved concentration (parameters included in Table 36 were necessary for its computation) is then used for comparison with $PNEC_{water}$.

In Table 36, those equations that have to be used to derived the $PEClocal_{water}$ are displayed. These equations were extracted from the TGD. In this table, if data is referred to as "data set" it means that the value was obtained from the industry or from experiments.

**Table 36. Parameters and equations necessary for the computation of $PEClocal_{water}$ for Example 1.**

| Parameter and Equation | Units | Value | Derivation |
|---|---|---|---|
| $PEClocal_{water} = Clocal_{water} + PEC_{regtonal,water}$ | [µg/L] | 0.031 | Eq. 48 TGD |
| $Clocal_{water} = \frac{Clocal_{eff}}{(1 - Kp_{susp} \cdot SUSR_{water} \cdot 10^{-6}) \cdot DILUTION}$ | [µg/L] | 0.00353 | Eq. 45 TGD |
| $Clocal_{eff} = Clocal_{inf} \cdot F_{STP\ water}$ | [mg/L] | 0.0000329 | Eq. 33 TGD |
| $Clocal_{inf} = \frac{Elocal_{water} \cdot 10^6}{EFFLUENT_{STP}}$ | [mg/L] | 0.0001646 | Eq. 32 TGD |
| $Elocal_{water} = F_{mainsource} \frac{1000}{T_{emission}} RELEASE_{water}$ | [kg/d] | 0.000329 | Eq. 5 TGD |

**Table 36. (continued).**

| Parameter and Equation | Units | Value | Derivation |
|---|---|---|---|
| $RELEASE_{water} = PRODVOL \cdot EF_{water}$ | [t/year] | $9.88 \cdot 10^{-5}$ | Data set |
| $EFFLUENT_{STP} = CAPACITY_{STP} \cdot WASTEW_{inhab}$ | [L/d] | $2 \cdot 10^{6}$ | Eq. 34 TGD |
| $Kp_{susp} = F_{oc} \cdot K_{oc}$ | [L/kg] | 4540 | Eq. 23 TGD |
| $PEC_{regional,water}$ | [µg/L] | 0.028 | EUSES v.2.03 |
| $F_{STP\ water}$ | [-] | 0.2 | TGD (1) |
| $F_{mainsource}$ | [-] | 1 | App. IB TGD |
| $T_{emission}$ | [d/year] | 300 | App. IB TGD |
| $PRODVOL$ | [t/year] | 197.5 | Data set |
| $F_{water}$ | [-] | $0.5 \cdot 10^{-6}$ | Data set |
| $CAPACITY_{STP}$ | [eq.] | 10000 | Table 9 TGD |
| $WASTEW_{inhab}$ | [L $d^{-1}$ $eq.^{-1}$] | 200 | Table 9 TGD |
| $F_{oc\ susp}$ | [$kg_{oc}/kg_{solid}$] | 0.1 | Table 5 TGD |
| $K_{oc}$ | [$L/kg_{oc}$] | $4.54 \cdot 10^{-4}$ | Data set |
| $SUSP_{water}$ | [mg/L] | 15 | Table 5 TGD |
| $DILUTION$ | [-] | 10 | TGD |

(1) Assuming it is connected to a municipal sewage treatment plant.

Note: green rows refer to parameters derived from others; red rows refer to input parameters assumed or available from data sets.

Nomenclature:

| | |
|---|---|
| $PECloca_{water}$ | Predicted environmental concentration during episode |
| $Cloca_{water}$ | Local concentration in surface water during episode |
| $Cloca_{eff}$ | Concentration of the substance in the STP effluent |
| $Cloca_{inf}$ | Concentration in untreated wastewater |
| $Eloca_{water}$ | Local emission rate to (waste) water during episode |
| $RELEASE_{water}$ | Release to the water compartment |
| $EFFLUENT_{STP}$ | Effluent discharge rate of STP |
| $Kp_{susp}$ | Solids-water partitioning coefficient of suspended matter |
| $PEC_{regional,water}$ | Regional concentration in surface water |
| $F_{STP\ water}$ | Fraction of emission directed to effluent by STP |
| $F_{mainsource}$ | Fraction of release at the local main source at a given life-cycle stage |
| $T_{emission}$ | Total number of days for the emission at a given life-cycle stage |
| $PRODVOL$ | Production volume of the substance |

| | |
|---|---|
| $F_{water}$ | Fraction of tonnage released to the water compartment |
| $CAPACITY_{STP}$ | Capacity of the local STP |
| $WASTEW_{inhab}$ | Amount of wastewater per inhabitant |
| $F_{oc\ susp}$ | Weight fraction organic carbon in susp. solids |
| $K_{oc}$ | Partition coefficient organic carbon-water |
| $SUSP_{water}$ | Concentration of suspended matter in the river |
| $DILUTION$ | Dilution factor |

In the TGD it is mentioned that, according to Regulation 793/93, three different conclusions may apply on the basis of the risk characterization:

- Conclusion (i) There is need for further information and/or testing.
- Conclusion (ii) There is at present no need for further information and/or testing and no need for risk reduction measures beyond those which are being applied already.
- Conclusion (iii) There is a need for limiting the risks; risk reduction measures which are already being applied shall be taken into account.

It is also mentioned that if the PEC/PNEC ratio is found to be less than or equal to one for a given compartment, conclusion (ii) shall apply. Therefore, in this example conclusion (ii) should be drawn for this compartment at this local site because the PEC/PNEC ratio is <1 (see Table 37).

**Table37. Risk characterization for Example 1.**

| Parameter | Units | Value | Derivation |
|---|---|---|---|
| $PEClocal_{water}$ | [µg/L] | 0.031 | Eq. 48 TGD |
| Lowest $NOEC_{water}$ | [µg/L] | 3.1 | Table 9 (this document) |
| Assessment factor to derive $PNEC_{water}$ | [-] | 10 | Table 16 TGD |
| $PNEC_{water}$ | [µg/L] | 0.31 | Assessment factor and data set (1) |
| $\frac{PEClocal_{water}}{PNEC_{water}}$ | [µg/L] | 0.10 | Table 32 TGD |

**Example 2**

*Risk characterization of the occupational exposure to HBCDD through the use of fine powder in textile backcoating (according to ECB (2008), scenario ADDING. Industrial use of HBCDD as an additive).*

Measured data for the use of fine powder HBCDD in textile backcoating produced for one plant was considered to be representative for the textile backcoaters (Searl and Robertson, 2005). The results of this study indicated that during backcoating with an active use of HBCDD, the total mean and 90$^{th}$ percentile air concentration were 1.4 and 3.1 mg/m$^3$, respectively. The value of 3.1 mg/m$^3$ was directly used in the risk characterization as a risk worst-case concentration for the inhalation exposure. For this exposure route, calculated MOS are shown in Table 38 together with the PTDI values used for their computation.

Dermal exposure to HBCDD was assessed with the software EASE (Estimation and Assessment of Substance Exposure) and then converted to mg/kg/day by considering the general characteristics included in Table 38. PTDI values were the same as for the inhalation exposure scenario and resulting MOS are also contained in Table 38.

**Table 38. Occupational exposure to HBCDD through the use of fine powder in textile backcoating.**

| | |
|---|---|
| **General characteristics of the scenario** | |
| Body weight | 70 kg |
| Ventilation rate | 10 m$^3$/day |
| Dermal absorption | 4% w/w |
| **Specific characteristics of the INHALATION exposure scenario** | |
| *Exposure$_{inhalation}$ (mg/m$^3$)* | *3.1 mg HBCDD/m$^3$ (experimental data)* |
| *Exposure$_{inhalation}$ (mg/kg/day)* | *0.44 mg/kg/day* |
| **Specific characteristics of the DERMAL exposure scenario** | |
| Dermal exposure to textile dust | 0-0.1 mg/cm$^2$/day (EASE software) |
| Surface of the exposed areas | 1200 cm$^2$ (hands + face) |
| *Exposure$_{dermal}$ (mg/day)* | *120 mg HBCDD/day* |
| *Exposure$_{dermal}$ (mg/kg/day)* | *0.07 mg/kg/day* |
| **Provisional tolerable daily intakes (for different endpoints)** | |
| PTDI$_{repeated\ dose\ toxicity}$ | 22.9 mg/kg/day |

| | |
|---|---|
| $PTDI_{reproductive\ toxicity}$ | 10 mg/kg/day |

**Table 38. (continued).**

| **REPEATED DOSE TOXICITY - Margins of safety (for different exposure routes) (1)** | |
|---|---|
| $MOS_{inh.,\ repeated\ dose\ toxicity}$ | 52 (>20) |
| $MOS_{dermal,\ repeated\ dose\ toxicity}$ | 327 (> 20) |
| $MOS_{multiple\ routes,\ repeated\ dose\ toxicity}$ | 45 (> 20) |
| **REPRODUCTIVE TOXICITY - Margins of safety (for different exposure routes) (1)** | |
| $MOS_{inh.\ reproductive\ toxicity}$ | 23 (< 50) |
| $MOS_{dermal\ reproductive\ toxicity}$ | 143 (> 50) |
| $MOS_{multiple\ routes,\ reproductive\ toxicity}$ | 20 (< 50) |

(1) Minimal MOS for repeated dose toxicity = 20; Minimal MOS for reproductive toxicity = 50

When comparing calculated MOS values with a minimal MOS of 20 for repeated dose toxicity, it can be observed that there is no concern for the inhalation and dermal exposure. Therefore, conclusion (ii) could be drawn for these two cases.

When comparing with a minimal MOS of 50 those MOS values obtained for reproductive toxicity, it can be stated that there is concern for the inhalation exposure (and consequently for the multiple route exposure), but not for the dermal one. Thus, for reproductive toxicity, conclusion (ii) could be drawn in the case of dermal exposure and conclusion (iii) in the case of inhalation exposure.

**Example 3**

*Risk characterization of the occupational exposure to HBCDD through the industrial end use of products containing HBCDD (according to ECB (2008), scenario SEWING (occupational). Industrial end-use).*

For this scenario, according to ECB (2008), there are no measured data on inhalation exposure or dermal exposure during the industrial end use of products containing HBCDD. Given this situation, a possible scenario had to be set. The characteristics of this scenario are given in Table 39, and the resulting MOS.

**Table 39. Occupational exposure to HBCDD through the industrial end use of products containing HBCDD.**

| | |
|---|---|
| **General characteristics of the scenario** | |
| Action | A textile worker is sewing flame retarded textiles with backcoating |
| Concentration of HBCDD | 25% v/v HBCDD |
| Working period | 8 h/day |
| Body weight | 60 kg (many textile workers are women) |
| Ventilation rate | 10 $m^3$/day |
| Dermal absorption | 4% w/w |
| **Specific characteristics of the INHALATION exposure scenario** | |
| Concentration of airborne textile dust | 5 mg/$m^3$ |
| Concentration of HBCDD in the material and in the airborne dust | 10 % w/w |
| *$Exposure_{inhalation}$ (mg/$m^3$)* | *0.5 mg HBCDD/$m^3$* |
| *$Exposure_{inhalation}$ (mg/kg/day)* | *0.08 mg/kg/day* |
| **Specific characteristics of the DERMAL exposure scenario** | |
| Dermal exposure to textile dust | 1 mg/$cm^2$/day |
| Surface of the exposed areas | 840 $cm^2$ (hands) |
| Concentration of HBCDD in the material and in the airborne dust | 10 % w/w |
| *$Exposure_{dermal}$ (mg/day)* | *84 mg HBCDD/day* |
| *$Exposure_{dermal}$ (mg/kg/day)* | *0.06 mg/kg/day* |
| **Provisional tolerable daily intakes (for different endpoints)** | |
| $PTDI_{repeated\ dose\ toxicity}$ | 22.9 mg/kg/day |
| $PTDI_{reproductive\ toxicity}$ | 10 mg/kg/day |
| **REPEATED DOSE TOXICITY - Margins of safety (for different exposure routes)** [(1)] | |
| $MOS_{inh.\ repeated\ dose\ toxicity}$ | 45.8 (> 20) |
| $MOS_{dermal\ repeated\ dose\ toxicity}$ | 382 (> 20) |
| $MOS_{multiple\ routes,\ repeated\ dose\ toxicity}$ | 164 (> 20) |
| **REPRODUCTIVE TOXICITY - Margins of safety (for different exposure routes)** [(1)] | |

| | |
|---|---|
| $MOS_{inh.\ reproductive\ toxicity}$ | 125 (> 50) |
| $MOS_{dermal\ reproductive\ toxicity}$ | 167 (> 50) |
| $MOS_{multiple\ routes,\ reproductive\ toxicity}$ | 71 (> 50) |

(1) Minimal MOS for repeated dose toxicity = 20; Minimal MOS for reproductive toxicity = 50

When comparing calculated MOS values with a minimal MOS of 20 for repeated dose toxicity, it can be observed that there is no concern for the inhalation and dermal exposure. Therefore, conclusion (ii) could be drawn in these two cases.

For reproductive toxicity, when comparing with a minimal MOS of 50, it can be stated that there is no concern for the inhalation and dermal exposure. Thus, for reproductive toxicity conclusion (ii) could also be drawn.